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STUDIES IN "STANDARD SAMPLES" OF SILICATE ROCKS AND MINERALS 1969-1982

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Critical Reader

J.A. Maxwell

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Foreword

My first contact with the problems in evaluating reference samples of rocks was in 1951 when a paper appeared in Analytical Chemistry (Schlecht, 1951) giving an outline of the data collected on the two rocks, G-1 and W-1, material subsequently described in detail by Fairbairn et al. (1951). Among the first few geologists I met, the opinion was expressed that the highly disparate data must have created many "red-faced chemists". My reply was that it was the geologists who should have been red-faced for having lived so long in a fool's paradise!

My first more direct involvement occurred some 18 years later, when, with the daring of ignorance, I undertook to derive values for the major and minor constituents of six U.S. Geological Survey samples for which Flanagan (1969) had published a rather comprehensive compilation. The exercise proved salutary as it also opened my eyes to some of the pitfalls in such work.

Several years later, I undertook the evaluation of six South African samples, at least one of them being of highly unusual composition (Russell et al., 1972).

By 1973, I had acquired enough skill and understanding to pretend to be an expert in the subject, and was quite ready, later in the same year, when I was asked to undertake an evaluation of two Canadian rocks, SY-2 and SY-3. Those samples (and MRG-1 which I managed to include with them) had been available for several years but had never been subjected to systematic collaborative analysis. So there I was, getting into things at an earlier stage than was the case with the USGS samples, namely soliciting analyses, collecting the data and evaluating all three samples. It was not until 1981, when work began on the Canadian iron formation rocks, that I was enabled to participate in a program beginning with the original raw material.

So, in a sense, my experience in this field was acquired in a reverse direction: first, evaluating samples from published compiled data; second, collecting and compiling data on existing samples; finally, participating in the selection and preparation of the samples themselves. In another sense, my experience has recapitulated the technological changes of recent years: the first set of calculations was done with a slide rule, later operations with increasingly sophisticated electronic calculators. Most recently, a computer program was devised by my colleague, R.M. Rousseau, to lessen the burden of computation. However, the large degree of subjectivity in all versions of my evaluation method has limited the usefulness of computing devices. That was deliberate, mainly to overcome the temptation to depend blindly on mathematical formulas to the detriment of knowledgeable understanding of the analytical processes. In simpler terms: it takes more than arithmetic!

Ottawa
4 April 1983

Sydney Abbey

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42 ASK – Analytisk Sporelement Komite (Scandinavia)
43 IRSID – Institut de Recherches de la Sidérurgie (France)
43 CRPG – Centre de Recherches Pétrographiques et Géochimiques (France)
43 ANRT – Association Nationale de la Recherche Technique (France)
43 GIT-IWG – Groupe International de Travail / International Working Group (France)
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45   ANRT I
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49   GIT-IWG
50   Other GIT-IWG materials
51 IAEA – International Atomic Energy Agency
52 IGB – Institute of Geology, Bulgaria
52 UNS – Ustav Nerostnych Surovin (Czechoslovakia)
53 ZGI – Zentrales Geologisches Institut (East Germany)
55   'International standard samples'

55 "National standard samples"
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STUDIES IN "STANDARD SAMPLES" OF SILICATE ROCKS AND MINERALS

1969 - 1982

Abstract

The historical development of "standard samples" of silicate rocks, minerals, and compositionally similar materials is reviewed, with particular emphasis on methods for resolving conflicting data to arrive at most probable composition values. Contributions of the Geological Survey of Canada's laboratories are described in detail. A critical review of available reference materials is presented, classified by originating institutions, ranging from new samples still undergoing evaluation, through evaluated samples in current use, to older samples whose supplies are largely exhausted. Detailed compositional information is presented for all samples (where available), with some indications of degrees of reliability of particular values. Better-established values are also listed in "concentration ladders", in which individual samples are listed in descending order of concentration for every constituent.

Résumé

Le bilan du travail fait sur les "échantillons standards" des roches et des minéraux silicatés, ainsi que des matériaux de composition similaire, est examiné. Un accent particular est mis sur les méthodes pour résoudre le problème des données contradictoires, afin d'obtenir les valeurs de composition les plus probables. La contribution de la Commission géologique du Canada est présentée en détail. Est inclus également dans ce bilan une critique sommaire sur les matériaux de référence actuellement disponibles, classifiés selon leur provenance et comprenant les nouveaux échantillons non évalués, ceux déjà évalués et utilisés partout, ainsi que les anciens échantillons presque tous épuisés. Des renseignements détaillés sont fournis sur la composition de tous les échantillons (lorsque disponsibles), ainsi qu'une discussion sur la fiabilité de certaines valeurs particulières. Les valeurs "bien établies" sont énumerées sous forme d' "échelles de concentration", dans lesquelles on retrouve les échantillons arrangés en ordre décroissant des teneurs de chacun des composants.

PART I

EVOLUTION OF THE SUBJECT

INTRODUCTION

The expression "reference samples", as used in this work, does not convey a very clear meaning. Others have preferred more assertive terms, such as "standard rocks", but as will be shown below, that term implies a greater degree of reliability and confidence than can realistically be expected in the case of rocks. It has been stated (Abbey, 1977a) that terms like "standard rocks" or "standard samples" may conjure up questionable comparison with, say, the Standard Kilogram or the Standard Metre. Although those true standards have now been replaced by standards based on fundamental physical parameters (e.g. the wavelength of a particular spectrum line of a particular isotope), the reliability of so-called "standard rocks" has never attained a level comparable to that of the Standard Kilogram or the Standard Metre, nor is it likely that it ever will attain such a level.

What, then, is meant by the term "reference material" or "standard rock"? In analytical chemistry a "standard solution" is defined as one of accurately known composition – at least in terms of a specified solute or a measurable chemical reactant. Thus a standard solution of an acid is characterized by its normality in terms of hydrogen ion, a standard solution of iron in terms of its iron concentration. In the latter case, the solution can be prepared directly from pure metallic iron; the former case would require "standardization" by titration against a "primary standard" – perhaps pure sodium carbonate. In either case, the accuracy of results obtained in the analytical application of each standard solution, whether in titration or in calibrating an instrumental technique, would depend largely on the primary standard involved – in these cases, pure iron or sodium carbonate.

As long as analytical methods used were mainly gravimetric, titrimetric or visual colorimetric, one of the major subsequent applications of reference materials, namely the calibration of instrumental techniques, was hardly relevant. Even then, however, certain other applications were very important – i.e. the control of everyday analyses, the settling of disputes between buyers and sellers and the testing of proposed new analytical methods.

We may now define a reference sample as a material of a particular type whose content of one or more constituents is known with a degree of confidence adequate for its intended applications. Further, such material must be in a physical state similar to that of the unknowns to be analyzed. With rocks, minerals, ores and many other nonmetallic solids, the sample must therefore be converted to the form of a finely-divided, adequately homogeneous powder.

"ROCKS ARE DIFFERENT"

The validity of this title has been questioned by analysts working with ores and similar materials, perhaps even by some involved with rocks and minerals. It can be argued that an ore is merely a rock which contains recoverable quantities of one or more economically significant constituents. Analysis of such material, in practice, would involve determination of the economically significant constituents and probably also of those constituents which may affect the extraction process or may contribute undesirable impurities to the final product.

A proposed reference sample of such an ore would of course require evaluation of its contents of the same constituents as normally determined in everyday samples. The organizer of an evaluation program would have a choice of two general approaches (A third method, proposed by Ingamells (1978) is considered later in this paper):

a) The "in-house" method: assuming that the laboratory responsible for preparation of the material has a broadly based, highly competent and varied expertise in analytical techniques, all analytical evaluation is done there and there alone. Each desired constituent is determined by at least two mutually-independent methods and results of such analyses must be in close agreement before an acceptable value for the concentration of that constituent is recognized. Alternatively, a "definitive method", in the hands of two or more individual analysts, might be used.

b) The "collaborative" or "consensus" method: a number of laboratories with established reputations for reliability in the analysis of the type of material of interest are invited to contribute analytical data on the proposed reference material. Consensus or recommended values, often with confidence limits, are deduced statistically from the many results reported.

Method (a) has been used extensively by the U.S. National Bureau of Standards for a wide variety of "standard reference materials". The National Research Council of Canada used a similar approach in evaluating two samples of marine sediments (Berman, 1981). In many respects, this approach would appear to be ideal, but there are a few potential pitfalls.

Firstly, the concept of "mutually independent methods" must be examined closely. For example, if a certain constituent were determined by two independent techniques, say plasma emission spectroscopy and atomic absorption, one might ask whether two different techniques were used in dissolving the sample, whether similar or different methods of separation (if any) were involved and what means were used to eliminate or correct for possible interferences.

Secondly, the possible existence of inter-laboratory bias must not be overlooked. Most knowledgeable analysts are familiar with situations where even with rigorously standardized analytical procedures, marked differences can arise between results from different laboratories. Thus the evaluation of a proposed reference material, if based on analyses done in only one institution, may well be subject to some unpredictable bias. Similar reservations can be held regarding "definitive methods".

Method (b) is more commonly used than (a). In the case of an ore or any other commercial product or raw material, there are bound to be a number of laboratories, mainly in industry, that are not only thoroughly familiar and experienced with the analysis of the material concerned, but are also likely to have a financial stake in the reliability of the results. In such programs, the results reported by different laboratories are generally not identical to one another but may be expected to be sufficiently coherent for all practical purposes. Derivation of acceptable consensus values is then not very difficult. Procedures used to that end may vary in detail, but in principle most of them involve criteria for the rejection of outlying results and computation of a mean value from the remaining results for each constituent. In some cases, replicate analyses are done in accordance with an experimental design, resulting in a measure of the degree of homogeneity of the sample, verification of the "certifiability" of the deduced values and establishment of confidence limits (Sutarno and Faye, 1975).

The analysis of rocks and minerals for geological studies represents a different picture in many ways:

i) Most rock analyses are essentially "complete" in that all major (1-100 pct), all minor (0.01-1.00 pct) and as many trace (100 ppm and under) constituents as possible are generally required. Because of the wide variation in composition in silicate rocks, many common constituents may move from one to another of the above arbitrary categories in going from one sample to another. In all that follows, then, the term "major and minor" is meant to include SiO_2, TiO_2, Al_2O_3, Fe_2O_3, FeO, MnO, MgO, CaO, Na_2O, K_2O, H_2O^+, CO_2, P_2O_5, F, and S. "Traces" essentially cover the rest of the Periodic Table, including non-carbonate carbon and chlorine. (Note that H_2O^- is not mentioned because only by converting all results to the "dry basis" is it possible to make meaningful comparisons between results from different sources. Unfortunately, many analysts tend to ignore the relatively simple but potentially important determination of H_2O^-, leading to a significant source of error with some samples, about which, more later.)

ii) Generally speaking, rocks and many minerals are not materials of commerce. Analyses are usually performed as support to geological studies. Aside from considerations of professional pride, no rock analyst has as great a financial interest in the accuracy of his results as has an analyst in, say, a manufacturing or mining industry. Analysts in industry tend to be qualified chemists, spectroscopists or well-trained technicians with expertise in the handling of specific materials. Although many highly-qualified chemists, spectroscopists and technicians are engaged in rock and mineral analysis, a considerable proportion of such work is done as a "side-line" by earth scientists whose main concerns lie elsewhere, or even by graduate students in the earth sciences with limited knowledge or understanding of analytical principles. The recent rapid growth in analytical instrumentation – particulary in the use of micro-processer-equipped instruments – has helped in boosting productivity and has made feasible many operations hitherto considered difficult or impossible, but it has also lulled many scientists who should know better into a false sense of security and a blind faith in gadgetry without sufficient grasp of the principles of operation. Use of techniques based on various forms of spectroscopy has served to eliminate many of the tedious separation steps needed in more purely chemical methods, but no technique developed thus far is entirely free from interferences, a vital fact in the analysis of materials as variable in composition as are rocks. Advertising claims of some instrument manufacturers have not helped the situation either.

iii) Analytical data on rock samples reported in the literature generally reflect the analytical resources of the originating institution. Even analyses that appear "complete" at first glance almost always fail to include some significant trace elements. It would hardly be an exaggeration to say that no single analytical laboratory in any geological institution in the world is sufficiently well equipped to determine adequately all of the elements in rocks, in particular over the wide ranges of concentration at which they may occur.

In evaluating a proposed reference sample of a rock, it is desirable to establish acceptable values for as many constituents as possible, so it is virtually impossible for a single institution to acquire all the necessary data. The "in-house" method of evaluation is therefore impractical for rock materials. An apparent exception would appear to be the case of the marine sediment samples mentioned earlier, but although those samples are rock-like in composition, they have not been evaluated for all of their constituents, only for certain ones of environmental significance.

An inevitable result of the varied backgrounds of the contributing analysts in the collaborative evaluation of proposed reference samples of rocks is what can most simply be referred to as incoherent and imbalanced results. The reported values for each constituent tend to be highly variable, in distributions that are often far from normal. Further, the number of results reported varies widely from one constituent to another, reflecting the relative ease or difficulty of determination. The task of the compiler of such data is further complicated by the failure of many analysts to provide sufficient information on the analytical methods used. Mere mention of a technique of measurement (e.g. "spectrophotometry") or of separation (e.g. "ion exchange") does not reveal much about how the job was done. With materials as heterogeneous as rocks, the technique of sample attack (e.g. pelletization, fusion, acid treatment) is of vital importance – not to mention the nature of the flux in a fusion, the type of acid used in decomposition, etc. Mention of some critical parameters in an instrumental finish would be very useful, as would also be some word about techniques of data reduction, a critical factor in such systems as those involving X-ray fluorescence spectroscopy.

In summary, despite similarities in the compositions of the materials concerned, rock analysis differs drastically from the analysis of ores mainly because of the large number of constituents of interest and the varying backgrounds of the analysts involved. Collaborative programs for the analysis of proposed reference samples of rocks are therefore different in many respects from those involving ores.

HISTORICAL REVIEW

The history of reference samples of rocks may be thought of as having begun with a bombshell with a paper read at the Americal Chemical Society's 1951 Summer Analytical Symposium (Schlecht, 1951). It was followed by a more comprehensive report (Fairbairn et al., 1951) on what was intended as a "Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks". The bombshell aspect of that development concerned the widely disparate results reported by 34 analysts on two specially-prepared proposed "standard rocks", granite G-1 and diabase W-1.

The discrepancies should not have come as a surprise. Larsen (1938) had observed similar phenomena in a study of six amphiboles, each analyzed by two to four separate analysts.

To appreciate the reactions to and conclusions drawn from both studies, one must recall the state of the art of rock analysis as of the 1930s and 1940s. Essentially all major and minor element determinations were based on gravimetric, titrimetric and a few visual colorimetric methods, some of which had remained unchanged for the better part of a century. The time interval between the two studies saw the emergence of arc-emission spectroscopy as a technique for trace elements and the beginnings of flame photometry for the alkali metals. X-ray fluorescence was in its infancy; neutron activation had not yet been extensively applied; atomic absorption was entirely unknown. For many constituents, there was little choice in analytical methods.

Larsen (1938) expressed the hope that the quality of rock analysis, which he found wanting, could be improved. He noted that several of the collaborating analysts had completely ignored the presence of fluorine and its possible effects on the analysis, although those effects were evidently not the only cause of the discrepancies. Despite Larsen's hopes and those of later workers, a similar situation was reported many years later (Abbey, 1979) when many analysts reported only the usual rock constituents on two particular samples, despite their being informed that both contained significant concentrations of uranium, thorium and the rare earths. Evidently the hopes for the improvement in quality had gone for naught.

Schlecht (1951) rightly pointed out that "The conventional procedure .... is designed for a rock having the approximate composition of common granite". Yet many an analyst has blindly applied it to samples of very different compositions. Still, the experience of G-1 (and of many granites that followed) showed that wide disparities were possible even with samples in the "common granite" composition range. Schlecht also expressed the hope of improvement in analytical procedures; he even thought of the possibility of introducing "standard procedures". However, it is difficult to visualize a set of standard analytical procedures that would be applicable to the highly variable compositions that can occur in silicate rocks.

Further, Schlecht asserted that "It was impossible to control the practices of the collaborators ...." – a situation which continued in many subsequent collaborative programs, as mentioned above.

Schlecht appropriately also quoted Lundell (1933a) with "... the kind of work necessary to approach 'true composition' of a standard; the main work is not statistical, but involves the achievement of concordance by methods that are independent – as different as possible in their chemical nature". The knowledgeable contemporary analyst might amend the last few words to read "... their chemical and instrumental nature". In that paper (Lundell, 1933a) and in another (Lundell, 1933b), a number of opinions were expressed that are equally valid today, despite the passage of nearly a half century.

The shock-wave occasioned by the discordant results on G-1 and W-1 brought about much soul-searching and heated debate. Fairbairn and Schairer (1952) attempted to separate the issues of precision and accuracy from one another by synthesizing a "haplogranite glass" of accurately known composition, similar to that of G-1, and having it analyzed by a select group of the analysts who had worked on the two rocks, but results were inconclusive.

A second report on G-1 and W-1 (Stevens et al., 1960) listed additional analytical data and discussed some special problems. Later, Chayes (1969, 1970) and Vistelius (1970, 1971) continued to debate the relative importance of sample inhomogeneity and of inter-laboratory bias as sources of error. Finally, Flanagan (1976b) pointed out a number of unanswered questions concerning the preparation and analysis of the rocks, but concluded that, since both were by then depleted, they had best be "laid to rest" – hence his title: "G-1 et W-1: Requiescant in Pace!"

The 1960s saw a veritable proliferation of new "standard rock" samples from a variety of sources. The United States Geological Survey produced, during that decade and the '70s, a set of six ("USGS II") – AGV-1, BCR-1, DTS-1, G-2, GSP-1 and PCC-1; a further set of eight ("USGS III") – BHVO-1, MAG-1, QLO-1, RGM-1, SCo-1, SDC-1, SGR-1 and STM-1; and finally a set of three ("USGS IV") – BIR-1, DNC-1 and W-2. A number of additional samples are known to be in preparation or already prepared, but at this writing, nothing on them has been published.

In collaboration with the Association of Exploration Geochemists, the U.S. Geological Survey has also produced a suite of six reference samples, GXR-1 to -6 inclusive.

The Department of Geology, Queen Mary College, University of London, U.K., produced four reference rocks: I-1, I-3, M-2 and M-3. A committee representing several Scandinavian countries (Analytisk Sporelement Komite) produced samples ASK-1 and -2.

A French group, acting at first on behalf of the Centre de Recherches Pétrographiques et Géochimiques and later for the Association Nationale de la Recherche Technique, first produced GR; then BR, GA and GH; followed by Mica-Fe and Mica-Mg; then BX-N, DR-N, DT-N and UB-N; followed by VS-N, FK-N, GS-N and GL-O. Sometime later came AN-G, BE-N and MA-N. Several other samples are known to be in preparation at this writing.

The International Atomic Energy Agency produced, comparatively recently, SOIL-5 and SL-1.

The Zentrales Geologisches Institut, in East Berlin, first produced BM, GM and TB; later FK, GnA, SW and TS. The Department of Mineralogy, Leningrad State University prepared a sample merely described originally as "Khibiny-Generalnaya", but identified in the laboratories of the Geological Survey of Canada as NS-1. Somewhat later, the Institute of Geochemistry, Irkutsk, produced SG-1A, SGD-1A and ST-1A. The Institute of Mineral Raw Materials, in Czechoslovakia, prepared SS and KK.

In the intervening years, the Geological Survey of Japan produced JB-1 and JG-1, followed some years later by JA-1 and JB-2. The Mineral Resources Division, of Tanzania, was one of the earliest producers of rock reference samples with their T-1.

The National Institute for Metallurgy, of South Africa, is one of the major sources, with NIM-D, NIM-G, NIM-L, NIM-N, NIM-P and NIM-S. At this writing, fourteen additional samples are undergoing evaluation.

More details on the history, description and evaluation of the above and other samples are given in a later part of this report.

THE CANADIAN EXPERIENCE

A major factor in the preparation of Canadian reference samples of rocks and rock-like materials has been the Canadian Certified Reference Materials Project (CCRMP), now an activity of the Canada Centre for Mineral and Energy Technology, a branch of the Department of Energy, Mines and Resources Canada, but also involving a number of additional organizations in government (federal and provincial), industry, and universities. The Project evolved from the original Non-Metallic Standards Committee of the then Canadian Association for Applied Spectroscopy (CAAS, now the Spectroscopy Society of Canada). Scientists of the then Mines and Geological Survey branches of the then Department of Mines and Technical Surveys played a major role in the founding of both the CAAS and its Standards Committee, and have continued active participation in the successor organizations.

By far the largest number of reference samples produced by the CCRMP have been ores of various types, largely in response to the needs of mining and metallurgical industries. The first rock samples, SY-1 and SU-1, appeared in the 1950s, to be followed later by SY-2, SY-3 and MRG-1, the last of these being a product of École Polytechnique, Montreal. More recently, SO-1 to SO-4 were processed for Agriculture Canada, BCSS-1 and MESS-1 for the National Research Council and LKSD-1 to LKSD-4, STSD-1 to STSD-4 and FeR-1 to FeR-4 for the Geological Survey of Canada.

"ORDER OUT OF CHAOS"

Although many of the later exercises in the preparation, collaborative analysis and evaluation of proposed reference samples of silicate rocks and minerals endeavored to avoid the errors and pitfalls encountered in the work on G-1 and W-1, the erratic pattern of analytical data persisted. Further, every originating organization appeared to have ideas of its own regarding the selection, crushing, grinding, sampling and analysis of the proposed reference materials, nor was there any consistency in the techniques used to evaluate the discordant data. Some published "provisional values" based on preliminary analyses that were not always of the best quality, only to find others quoting those values as "certified". Some originators published systematic compilations of analytical results but stopped short of suggesting "best values". Again, some ill-advised workers accepted the arithmetic mean of all published results for a given constituent as a firmly established value.

Many and varied were the statistical and pragmatic manipulations resorted to by those who did attempt to assign values on the basis of available analytical data. (Details follow in the next section of this report.) Perhaps most distressing of all was the failure to achieve consistency in nomenclature. Assigned values derived from collaborative results were described, with varying degrees of reliability as magnitudes, averages, recommended values, preferred values, accepted values, guaranteed values, certified values, attested values, best values, proposed values, most probable values, etc., etc. Worse still, nowhere in the literature were there definitions of the many different terms used.

If the originators of reference samples were lax in their practices and terminology, users were often guilty of failure to understand the limitations of published values, and of wasteful use of valuable reference materials. Many analysts and other users still seem to be unaware of the tremendous expenditure of time and effort involved in the production of reference samples.

The need for some co-ordination of information on reference samples was recognized when Taylor and Kolbe (1964) prepared a limited list of available materials. Flanagan and Gwyn (1967) presented a longer list, but did not distinguish between rocks and ore materials. The same was true of a later, more comprehensive list by Flanagan (1970).

Still later, Flanagan (1973) published a lengthy list of samples available from a half-dozen sources in as many different countries, complete with many "magnitude", "average" and "recommended" values – but again without defining those terms. Abbey (1975a) took issue with the validity and accuracy of some of Flanagan's (1973) values. Flanagan (1975) rejected some of the criticism but did publish a page of corrections.

Abbey (1972) listed some 18 different samples, most of them the same as in Flanagan (1973). Some of Abbey's values were based on those recommended by the originators of the samples, others on an early version of the "select laboratories" method (which is discussed in more detail below). Discrepancies between Flanagan's and Abbey's values led to the critical comment and reply (Abbey, 1975a; Flanagan, 1975) mentioned above.

In his next compilation, Abbey (1973) increased the count of samples to 34 and introduced the reduction of all data to the "dry basis" in order to put all samples on a similar, presumably reproducible footing. Subsequent compilations (Abbey, 1975b, 1977b, 1980) saw the number of samples listed increase to nearly 100 (now to 168) and improved means of presentation of the data.

The state of reference samples of geological materials became the subject of special symposia at international meetings in France in 1975 (Rubeska, 1977), in Czechoslovakia (Abbey, 1977c) and in South Africa (Steele, 1977a) in 1976, and at the Geoanalysis '78 Symposium in Ottawa in May 1978. Meanwhile, T.W. Steele, of the National Institute for Metallurgy, Randburg, South Africa, announced the formation of an International Study Group on Reference Materials (ISGRM) with an impressive list of members. At about the same time, K. Govindaraju, of the Centre de Recherches Pétrographiques et Géochimiques, Nancy, France, produced the first issue of a new journal, Geostandards Newsletter, with a Board of Regional Editors that included many who were members of the ISGRM.

The Geostandards Newsletter has served as a medium of exchange of information on geological reference materials. Papers have appeared to introduce new samples, to present new data on various samples, to discuss techniques of sample evaluation and other "standards theory", to describe analytical facilities in laboratories involved in the analysis of reference materials, to report on activities of the ISGRM, to report on discussions on reference materials at conferences, etc. The journal has brought many new members to the "geostandards community" and has seen the introduction of many new and innovative ideas.

Although the Geostandards Newsletter shows an impressive list of Regional Editors, most of the credit for its success must go to the Editor-in-Chief, K. Govindaraju. Only a handful of the regional editors have played on active role in the journal.

"THE GAMES PEOPLE PLAY"

The originators of reference samples of rocks have gone their own ways in the selection, collection, preparation, distribution and analysis of the materials. In all of those steps, as well as in the verification of homogeneity, there have been differences of detail, but most of the procedures followed have had much in common. The problem of arriving at acceptable consensus values from a mass of incoherent data has seen a highly varied series of approaches – seemingly as varied and incoherent as are the raw data.

To the casual observer, it would appear that an arithmetic average of all the results reported for a given constituent would give a close approximation of the truth, provided there were a sufficiently large number of results. The weakness of such an approach is clearly indicated in the first compilation on USGS II (Flanagan, 1969). Table 4 of that reference lists "Average of constituents normally determined in a rock analysis (per cent)". If those averages were a good approximation of the true concentrations of the rock-forming oxides and elements, their sum would be expected to lie close to 100 per cent. In fact, the sums varied from 100.12 for AGV-1 to 100.88 for PCC-1, even though many trace elements had not been included in the summation.

The average value for Fe_2O_3 in PCC-1 was given as 2.84_7 per cent, FeO as 4.94_8. If we re-calculate the average FeO to its Fe_2O_3 equivalent and add the average Fe_2O_3, we get 8.33_7 per cent as the total iron content, expressed as ferric oxide. However, the average value of all results for total iron, expressed as ferric oxide, was given as 8.53_7 per cent. Clearly something was wrong.

In the discussion which follows, various proposed attempts to overcome the above dilemma are described and compared. A set of actual data (nickel results for sample CCRMP-SY-3) are used to illustrate the characteristics of the various proposed measures, giving not only the various derived nickel values, but also the effect of each measure (when applied to all constituents) on the summation and on the comparison of the two possible derived values for total iron. The summation in each case includes all trace elements (converted to oxides, where appropriate) which can contribute 0.005 per cent or more to the total; the summation is also corrected for the oxygen equivalent of fluorine, sulphur and chlorine. The total iron content, expressed as ferric oxide, calculated from values for Fe_2O_3 and FeO derived from results reported for those two oxides is referred to as Fe_2O_3TC. The same constituent, derived directly from results reported as total iron, is referred to as Fe_2O_3TR. Closeness of the summation to 100 per cent and closeness of the two "total iron" oxides to one another may be regarded as measures of the validity of a particular derivation scheme. More details are given in the section on Comparisons.

It should be noted that neither the summation nor the iron-oxide compatibility should be regarded as infallible tests. Both have known limitations. Rock analysts are well aware of the hidden compensating errors that can be masked in a summation. In cases where major constituents have been determined by purely chemical means, it is possible that the content of some trace elements may be included in the results for some of the majors (e.g. strontium with calcium), so the inclusion of trace-element equivalents can produce high summations. Ferrous and ferric iron are determined only by wet chemical treatment, total iron by methods that may be purely chemical (e.g. oxidimetric titration), by methods involving chemical pre-treatment followed by instrumental measurement (e.g. atomic absorption) or by methods that may be entirely instrumental (e.g. X-ray fluorescence). Thus incompleteness of acid decomposition – a common failing in dealing with samples containing pyrite, chromite or other resistant minerals – can introduce a significant bias.

Although the limitations of both of the above validity tests cannot be overlooked, they are used in this work for want of anything better.

The raw data used in the comparisons that follow are presented in Table 1 (Abbey, 1979).

Means

If the arithmetic mean, or average, of a set of data does not represent a good approximation of the true value, can the cause be the presence of outlier values? In Table 1, for example, the 31 results appear to be nicely spaced in a fair, if not "normal" distribution, except for the very highest value, which is far removed from its nearest neighbor. Some workers have concluded, with some justification, that by applying statistical tests to eliminate outliers, the mean of remaining values should be closer to the truth than would be the mean of all available data. Thus Steele et al. (1978) rejected all values lying beyond three standard deviations of the overall mean as one way of eliminating outliers. Stepwise removal of extreme values with intermediate application of other tests were also used by Steele et al. – to a point where every test indicated that the remaining values satisfied an arbitrary criterion. The three tests used were measures of kurtosis and skewness (Ferguson, 1961a, b) and of the "a" statistic (Geary, 1935, 1936). Not surprisingly, the four different approaches did not always produce the same result.

It should be pointed out that Steele et al. (1978) were rejecting extreme outliers as a first step in a more involved procedure, not for merely calculating a "trimmed" mean. Details of their procedure are given below in the section describing Selective Approaches.

In a more direct approach to the elimination of outliers specifically aimed at attaining a trimmed mean, Dybczynski (1980) examined the performances of five possible tests: the coefficients of skewness and kurtosis (the same as used by Steele et al., 1978); the Dixon (1953) test, the Grubbs (1950) test, and the use of Student's "T" (Dixon and Massey, 1957). After finding that the last of these tests caused the elimination of too large a fraction of the available data points, Dybczynski settled on a scheme in which all of the four other tests were applied successively at the alpha = 0.05 significance level after the stepwise elimination of each end-member of the raw data, until a point was reached where no further, deletions were called for by any of the tests. He also suggested that any extreme outliers readily observed visually be deleted before attempting any of the tests.

Dybczynski then verified the validity of his approach (at alpha values of 0.05 and 0.01) by comparing his deduced values with those found by two other approaches: the Gamma transformation (Christie and Alfsen, 1977) and dominant cluster (Ellis et al., 1977) (both of which are examined more fully in the section on Modes), using analytical data on three "standard water" samples –

Table 1: Reported results for Ni (ppm), Sample CCRMP-SY-3

("Numerical histogram")

9								
9								
8.5								
8								
8								
8	14							
8	14							
7.4	14							
7	13.7							
7	12							
7	12	18						
6.9	11	17						
6.5	11	17						
5.2	10.	16.	.	24.	28.	34.	. . . .	125

presumably analyzed natural waters or synthetically prepared aqueous solutions. Dybczynski concluded that his procedure, working at the significance level of alpha = 0.05, gave results much closer to the true known values, and with much smaller uncertainty than did any of the others.

Subsequently, Dybczynski's method was applied to two rock-like reference materials issued by the International Atomic Energy Agency (IAEA), a soil (International Atomic Energy Authority, 1978; Dybczynski et al., 1979) and a lake sediment (IAEA, 1979). It is worth noting that neither of those materials had been subjected to either "complete" analysis or to ferric and ferrous iron determinations. It is therefore not possible to assess the validity of the published values by either the summation or iron-oxide compatibility tests mentioned above. It should not be forgotten, however, that a computation scheme that works well for a small number of trace elements in dilute aqueous solution will not necessarily be equally applicable to a solid system as complex as a silicate rock.

A somewhat simpler approach to the trimmed mean was that of Gladney (1980), who repeatedly rejected all values beyond three standard deviations of the mean, repeatedly applying the same test on the remaining values, until no more were rejected, then reported the mean and standard deviation of the remaining values. Gladney and Goode (1981) applied the procedure to data on a set of eight U.S. Geological Survey rocks, but Abbey (1982a) pointed out a number of conceptual errors and also indicated that Gladney and Goode had not fully utilized all available data. (Further details of the discrepancies involved are given in the section on USGS rocks.). Later, Gladney (1981) applied the procedure to the three Canadian rocks SY-2, SY-3 and MRG-1, using all data available in Abbey (1979). For the component in Table 1, he derived a value of 11, with an uncertainty of 4, in excellent agreement with the recommended value in Abbey (1979). However, when all of the values derived by Gladney were taken into account, the summations and iron-oxide compatibility tests compared unfavorably with those of Abbey, as shown in Table 2.

Long before any of the above schemes were proposed, various approaches were suggested for what might be called more drastic trimming of data – generally involving arbitrary deletion of all results lying beyond one, two or three standard deviations of the overall mean, with the mean of the remainder being taken as "best value".

Russell et al. (1972) suggested that results lying beyond three standard deviations of the overall mean be regarded as "rogue values" and should not be included in any attempt at determining a good approximation of the truth. However, they stopped short of suggesting that the mean of the remainder be regarded as a "best value". Flanagan (personal communication) suggested that many of his average or recommended values have been determined on a similarly trimmed population, but indicated that some subjective judgment was also involved.

Ando et al. (1974) listed "consensus means", defined as the arithmetic mean of the analytical values within two standard deviations of the overall mean for JG-1 and JB-1, but did not specifically recommend those values. Apparently, those values were considered to be a closer approach to the truth than an overall mean – but evidently little more than an approach.

Stevens and Niles (1960), after examining sources of error in (mainly conventional) rock analysis and studying several statistical options, concluded that the best approximation of "true value" would be the "preferred mean" – i.e. the mean of remaining values after eliminating those beyond one standard deviation of the overall mean. The same approach was recommended by Thomas and Kempe (1963). In a series of publications (Roubault et al., 1968; de la Roche et Govindaraju, 1969; 1971), the same general scheme was followed, but a measure of subjective judgement was also used – particularly for trace elements. Later on (Govindaraju, 1980), the same group modified their treatment of the data, as shown in the section on Selective Approaches.

If each of the above means – trimmed or otherwise – is applied to the data in Table 1, results are as follows:

Overall mean	16.0 ppm Ni
Mean, results beyond three standard deviations deleted	12.4
Mean, results beyond two standard deviations deleted	12.4
Mean, results beyond one standard deviation deleted	12.4
Mean, after two-cycle treatment of immediately preceding	10.8

It would appear that the trimming of populations is a desirable first step, at least, in approaching "best values", but there seems to be no consensus on where to stop. The general goal appears to be the attainment of a residual population that is normally distributed. However, with rock samples, it often happens that no amount of trimming will result in a symmetrical, let alone normal distribution. That fact led Sankar Das (1979) to conclude that better results would be expected if distributions were regarded as log-normal, where the geometric mean would then be considered as the best measure of true value. Applying that measure to the data in Table 1 yields a value of 11.9 ppm nickel.

Medians

Would the use of a median rather than of one of the various means described above provide more reliable "best values"? The magnitude of the median depends as much on the ranking of individual results in a population as it does on their numerical values. It is affected to only a small degree by the deletion of outliers. For that reason it is an attractive option, particularly as a first approximation and especially where the available raw data are too few in numbers to justify more elaborate treatment. It has the further advantage of being extremely simple to compute. The median of the data in Table 1 is 11 ppm nickel – again in close agreement with Gladney (1981) and Abbey (1979). If results beyond one, two or three standard deviations are deleted, the median becomes 10.5 ppm. A two-cycle, one standard deviation, deletion yields a median of 9.5 ppm.

Table 2. Summation and iron-oxide compatibility tests on three Canadian rocks

	SY-2		SY-3		MRG-1	
	SA[1]	ESG[2]	SA	ESG	SA	ESG
Sum	100.13	100.41	100.17	100.73	100.14	100.38
Fe_2O_3TC	6.28	6.40	6.42	6.56	17.85	18.05
Fe_2O_3TR	6.30	6.34	6.42	6.49	17.82	17.99

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[1] Abbey, 1979. [2] Gladney, 1981 (All figures in per cent, dry basis)

Modes

The tendency for the distribution of results for each constituent in a rock analysis to stray from normality has led some workers to consider the mode as a better measure than a mean or a median. However, just as there was no consensus on where to stop trimming in approaching the mean, there was no general agreement on how to estimate the mode. The five proposed schemes were as follows.

a. The Gamma Central Value, or Gamma Transformation Mode (GCV, GTM)

This approach was recommended by Christie and Alfsen (1977), who had earlier considered fitting a third-degree polynomial to the histogram of the data. Finding the polynomial fitting to be satisfactory only in the absence of extreme outliers, Christie and Alfsen turned to a data-transformation scheme which they believed "...may lead to more reliable estimates of 'true' concentrations than any other method..." they had tried.

In operation, the Gamma transformation involved an iterative routine in which varying values of a transformation parameter were applied until the skewness (as defined by a formula based on the variance) was reduced to an arbitrarily established low value. The originators favoured a limiting skewness of 0.001; Dempir (personal communication) found that stopping the iteration at a skewness of 0.05 made little difference to the final result; in our own work, we compromised at a limiting skewness of 0.01. Once the desired low level of skewness was attained, the mean and standard deviation of the transformed data were calculated and those values back-transformed, yielding the Gamma central value and the "higher and lower bounds" of confidence.

Thus the Gamma scheme suggested not only a means of establishing the best value in a skewed distribution, but also an asymmetrical measure of confidence limits. From a pragmatic point of view, it suffered from the disadvantage of requiring the use of a somewhat elaborate computer program. Christie kindly provided us with a copy of his program, but extensive modifications were needed to adapt it to our computation systems.

The Gamma central value of the data in Table 1 is 10.4 ppm nickel.

Some time after the paper of Christie and Alfsen appeared, Colombo (1980a) pointed out by a relatively simple argument that, in principle, the Gamma transformation mode was really the same thing as the median! Colombo's assertion was particularly striking inasmuch as determination of the Gamma transformation mode requires an elaborate computer program, while the median can be ascertained at sight, with no resort to any computing aid. Colombo admitted that the median and the Gamma central value are generally not identical but stated that the difference "...is not unexpected.... caused by the discrete rather than continuous distributions encountered in practice".

At this writing, Christie and Alfsen have issued no rebuttal to Colombo's challenge to their proposal, as far as the present writer is aware.

b. The Dominant Cluster Mode (DCM)

Ellis et al. (1977) proposed a simpler approach to the mode. It involved computation of the mean and standard deviation, deletion of values lying beyond four standard deviations of the mean and repeating the process using successively smaller multiples of the standard deviation, multiples that were asymptotic to unity. The process was stopped after either a fixed number of cycles had been performed, after a specified number of data points remained or after all remaining data points were identical. The mean of the remaining values was taken as dominant cluster mode. One of the tables in Ellis et al. (1977) listed 95-pct confidence limits of the mode but the method of computing them was given only as a reference to a private communication.

Some of the details of the procedure for finding the dominant cluster mode were slightly ambiguous (Abbey et al., 1979), but the resulting uncertainties had little effect on the final result.

The dominant cluster mode of the data in Table 1 is 8.8 ppm nickel – somewhat removed from the Gamma central value and from the means and medians given above. In other cases (Ellis et al., 1977; Abbey et al., 1979), the dominant cluster and Gamma transformation modes tend to be closer together.

c. The Moving Histogram Mode (MHM)

Abbey et al. (1979) pointed out that mere changes in the size of the class interval and in the location of class boundaries can drastically affect the shape of a histogram of analytical data, and hence the apparent characteristics of a distribution. Inasmuch as the highly-elusive mode is a product of the histogram, those authors proposed an arbitrary set of rules for the plotting of histograms in order that different distributions could be compared with one another on a common basis. They further suggested the plotting of a "moving histogram", in which the abscissa represented concentration and the ordinate represented the number of data points within a given concentration range from each data point itself. Rules were proposed for establishing the size of the concentration range interval. The abscissa of the point of maximum ordinate was taken as "moving histogram mode", with provision for resolving bi-modal distributions and other irregularities.

In its earliest application, the moving histogram mode appeared to fall quite close to the dominant cluster mode in all but a few cases. The MHM has the advantage over the DCM of being much simpler to calculate. In later work (Abbey, 1981a), involving many more constituents of three samples, the similarity of values of MHM and DCM was less pronounced. As a measure of best value, the MHM has been shown to be no better nor worse than the other modes.

The data of Table 1 yield a moving histogram mode of 8.00 ppm nickel.

d. The Moving Histogram Transformation Mode (MHTM)

As a simplified approach to the concept of data transformation (analogous to the determination of the Gamma central value), Abbey et al. (1979) proposed a scheme based on a geometric diagram in which a scalene triangle (corresponding to a skewed distribution histogram) was converted, point by point, to an isosceles triangle (corresponding to a symmetrical distribution). The mean of the transformed data was then back-transformed to give the "moving histogram transformation mode". Just as the MHM was found to fall close to the DCM, the MHTM fell close to the GTM. As was the case with the MHM, later work (Abbey, 1981a) tended to discredit the MHTM, both as an equivalent of the GTM and as a measure of best value.

When the MHTM computation is applied to the data in Table 1, the value found is 7.9 ppm nickel.

e. The Plot Method Mode (PMM)

Colombo (1980b) proposed another simplified approach to the mode. It involved arranging the data in order of magnitude and plotting each value as ordinate against its rank in the sequence as abscissa. The point of minimum slope was taken as "plot method mode". Colombo admitted difficulties with irregular distributions and proposed procedures to overcome such difficulties, procedures which left room for ambiguity. As modified by Abbey (1981a), the plot method yields a value of 7.4 ppm nickel from the data of Table 1, again rather far removed from the other measures. However, as pointed out by Abbey (1981a), the PMM does appear to have advantages over other measures, as outlined in the section on Comparisons.

Experimental Designs

As mentioned earlier, many collaborative analytical programs on proposed reference materials have been conducted according to experimental designs where each participating laboratory has been requested to do a specified number of replicate determinations of each constituent on portions taken from each of a specified number of containers of sample material. The number of subsamples per bottle and the number of bottles sampled have not been the same in all cases, but all have used the raw data in analysis-of-variance calculations from which it has been possible to assess the degree of homogeneity of the samples, whether or not available results are sufficiently concordant to establish firm values and to set confidence limits on the derived values (Sutarno and Faye, 1975). However, in most if not all cases, the actual derived values were the means of reported results (or the means of the means reported by participating laboratories) after trimming off outliers detected empirically or by means of one or more statistical tests.

The use of such schemes is highly commendable at least for the laboratories of the issuing agency. Such practices appear to be the rule in many operations involving ores. But, remembering that "Rocks Are Different", the question arises whether such approaches might not lead to a law of diminishing returns. Some reasons for such a question follow.

The report edited by Flanagan (1976a) is probably the best example of the application of experimental design to rock reference samples. In some 22 papers included in that compilation, data are presented on a variable number of constituents on anywhere from one to eight of the samples making up USGS III. The results appear to indicate that: (a) the samples are essentially homogeneous for most practical purposes; (b) where the "F" ratio indicates a significant difference between within-bottle and inter-bottle variances, the difference may be due more to too great concurrence of within-bottle results than to too great differences in results between bottles; (c) inter-laboratory factors seem to predominate as the root cause of discrepancies; (d) nowhere is there any indication of most probable values.

A specific weakness of schemes based on such designs (as published thus far) is the failure to account for skewed distributions, although there is nothing to prevent the use of data from such designs in derivation schemes designed to resolve skewed data.

From a purely pragmatic point of view, there are serious impediments to the implementation of a designed sampling scheme in the collaborative analysis of rocks and similar materials in which many constituents must be determined. Many laboratories who are sincerely interested in playing their part in such operations find that the extra work involved must be crowded in among their regular assignments, often with insufficient time available to give the work the special care it deserves. An example of the result of such conditions may be found in Bowman et al. (1979). All participating laboratories were requested to take five subsamples from each of two separate bottles of each of four soil samples and to determine as many constituents as possible in each subsample. Although a majority of the contributors reported the required 10 results for each constituent, some failed to identify the bottle represented by each result. Others reported anywhere from two to twelve results. Although all participants reported "method", there was evidence of bimodal tendencies in some distributions, regardless of method used. That was particularly true where "method" was "AA" – possibly because there was inconsistency in the techniques of sample attack. All involved may have measured a particular element with excellent precision and accuracy, but some were evidently not measuring all of that element in the sample.

Another case of confusion regarding methods occurred in another operation, where an analyst reported his method for carbon dioxide as "vol". Did he mean volatilization or volumetric? If the latter, was he titrating or measuring a volume of gas? Most important of all, did he evolve carbon dioxide by acid treatment (thus determining carbonate carbon) or by combustion (to determine total carbon)?

Organizers of collaborative analyses have had many bitter experiences with contributors who fail to satisfy all the requirements of the program without the added demand for systematic replication. Simply put, an analyst who is invited to provide data on, say, four or six samples, is more likely to accept the invitation than he would be if replicate sampling multiplies his workload by a factor of six or ten! With the large number of constituents required in rocks and the variable expertise available in various laboratories, the organizer of a collaborative program can hardly afford to sacrifice the potential contribution of any interested analyst.

Thus we have here still another of the various factors that contribute uncertainties to the usefulness of reference samples of rocks.

SELECTIVE APPROACHES ("WHEN COMMON SENSE SEASONS STATISTICS")

Shakespeare (1623) used the expression "...when mercy seasons justice...", implying that even a rigorously organized system must on occasion be applied with consideration of special circumstances. Similarly, many of those who work with the problems of unravelling the composition of rock reference samples from highly discordant raw data have come to believe that rigorous statistical treatment will not always provide the best answers. Those who persist in adhering to what they consider sound mathematical procedures often appear to be blinded by the very figures in the raw data. They tend to ignore (or to fail to understand) the uncontrolled variables involved, of which those mentioned in the preceding section represent only a few.

Those who appreciate the uncertainties involved in the reported results have resorted to various approaches to overcome the limitations in the application of orthodox statistics. The essential validity of statistical methods are not in question; it is just that the unknown factors behind the raw data hardly justify such precise treatment. (One does not measure the diameter of a dumpling with a micrometer!)

Two broad types of "selective" approaches have been proposed: a choice between various statistically derived measures and the restriction of calculations to data reported by a small number of laboratories whose work appears to be superior to most of the others.

Choice between statistical measures

In an apparent acknowledgment of the limitations of purely statistical derivation of best values, Steele et al. (1978) first introduced the idea of a subjective or knowledgeable choice among various statistically derived measures for each constituent. In that case, they computed two trimmed means, the median and dominant cluster mode. In a later set of calculations (Steele and Hansen, 1979), the same group also compute the Gamma central value and the "Gastwirth median" (Gastwirth, in Andrews et al., 1972, p. 8). In both cases, they chose one of the various computed estimators and recommended that value – in some cases after some rounding.

Later, Govindaraju (1980) used a similar approach, computing the overall arithmetic mean, a trimmed mean, the median, Gamma central value, dominant cluster mode, geometric mean and even a "preferred mean of central values" (counting all of the foregoing except the overall arithmetic mean), and recommending a value by judicious choice among them.

It is to the credit of both of the above groups that they recognized the limitations of the computational measures they had used earlier and accepted the necessity to inject subjective judgment into the choice of a "best value". Govindaraju had already made use of limited subjective judgment in his earlier work (e.g. de la Roche and Govindaraju, 1969).

In another case, the subjective judgment was in a choice as well, but one between actual results rather than between statistical estimators. It concerned the three Scandinavian samples ASK-1, -2 and -3 (of which only the first two may be considered rocks) (Christie, 1975). Only a limited number of trace elements were of interest and all of the analyses were done in contiguous countries. It was then a simple matter to bring all participating analysts together to discuss the relative merits of the various results and to arrive at a consensus. A major advantage of such an arrangement is the opportunity for the participants to explain more fully to one another any details of their methods that might be of use in evaluating the results. Unfortunately, it would hardly be practical to operate in that manner where more-or-less complete analyses are required and the participants are scattered all over the world.

Restriction to Specific Laboratories

Ingamells (1978) suggested that the "round-robin" collaborative analysis approach was a waste of time and effort. He proposed instead that only two mutually independent analysts, working in different laboratories and presumably using mutually independent methods, be required to analyze proposed reference materials. Where there is close agreement in the results reported by two such reputable analysts, there can be little doubt of the "true" value. Where the two fail to agree, Ingamells proposed that a third party be called in to resolve the differences. (What would happen if all three failed to agree was not made clear – presumably it would involve a fourth or more participants, if necessary).

When a somewhat modified Ingamells approach (see section on Comparisons) was applied to the data in Table 1, the result was 10 ppm nickel.

It is likely that Ingamells' proposal would work well with ores or similar materials where only a few constituents are of interest – and where laboratories with suitable competence are known to exist. But again, with rocks, we are faced with the need to determine so many constituents and with the highly variable competence of available laboratories. Doubtless two laboratories could be found which can produce excellent results for, say, silica. Would they be equally competent to produce good results for traces of gallium? Perhaps not. If one is obliged to select a large number of laboratories in order to achieve adequate coverage for so many elements, one might as well have all of them report as many constituents as they can.

The other approach to the use of data from a limited number of sources, – the "select laboratories" method – was originated, modified and adapted by the present writer. Its evolution may be regarded as the backbone of his experience in this field and is therefore described in detail in the next section of this report.

THE SELECT LABORATORIES METHOD

"Theory"

This method is founded on the assumption that inter-laboratory factors are the prime cause of discrepancies in analytical data from collaborative programs. As mentioned earlier, Chayes (1969, 1970) and Vistelius (1970, 1971) debated the relative importance of inter-laboratory factors vis-à-vis inhomogeneity but came to no agreed conclusion. Both used reasoning based on statistical principles. However, in view of conclusions drawn earlier in this paper, namely that the uncontrolled and unquantifiable sources of error in collaborative analysis of rocks cast doubt on the validity of such reasoning, it may not be surprising that Chayes and Vistelius could not resolve their differences.

On the other hand, Snavely et al. (1976), Tatlock et al. (1976) and Walker et al. (1976) subjected three samples (a nepheline syenite, a rhyolite and a quartz latite) to spectrographic analysis for minor and trace elements in laboratories then located in Washington, D.C., in Denver, Colorado, and in Menlo Park, California. Each bulk sample was first split into thirds; each laboratory was provided with one bottle from each third of each sample and was requested to analyze two subsamples out of each bottle. Analysis of variance computations revealed that for the 13 elements determined in the syenite, eight showed significant differences between laboratories, none between bottles. For the eleven elements determined in the rhyolite, the corresponding figures were four and none out of eleven. For the quartz latite, out of 13 elements, six showed significant differences between laboratories, only one between bottles. Combining the data for the three samples, we have only one indication of inter-bottle differences, 18 of inter-laboratory differences, out of a possible 37.

Bearing in mind that all three of the laboratories were part of the U.S. Geological Survey and hence that their analytical procedures were probably similar to one another, if not identical, one cannot deny this strong evidence of the importance of inter-laboratory bias as a fact of life in collaborative or "round-robin" operations.

Smet and Roelandts (1978), in comparing their neutron activation results on two ultrabasic reference rocks with data reported by other analysts, observed that "...most analysts have analyzed both PCC-1 and DTS-1 and that very often the same laboratories report consistently high or low values for a given element in both the samples". They concluded that "...examination of the analytical methods employed seems appropriate". Had those authors then looked into the identification of each result in terms of contributing laboratory rather than of method, they might have detected more significant support for their earlier observation regarding inter-laboratory factors. As mentioned earlier, mere listing of "method" involved in particular results can be highly misleading because the methods referred to are generally merely techniques of measurement; details of sample pre-treatment or of means for overcoming interference effects can differ widely among different laboratories. Thus results obtained from two different laboratories by, say, X-ray fluorescence, can involve sufficient differences in procedural detail as to bring about greater discrepancies between the two than there might be between either one and, say, neutron activation results from one or the other of the same laboratories, or from a third.

It would appear that Smet and Roelandts assumed that each laboratory used a particular method, but in any case, their observations lend some support to the assumption of the importance of inter-laboratory factors.

Morrison (1980) mentioned three interesting cases where interlaboratory bias played a major role. One concerned the determination of impurities in uranium during early work on nuclear energy in the Second World War, another the analysis of lunar rocks, and the most recent, the analysis of volcanic ash from the eruption of Mount St. Helens.

Quoting Morrison: "The controversy was finally resolved by having the chemists from the different laboratories work through the procedures together in the same laboratory. Lo and behold, systematic errors suddenly became apparent to all." (This concerned the Manhattan Project.)

In the Apollo Lunar Analysis Program, Morrison stated: "Wide ranges in concentration had been reported for the various elements, and the study assessed the influence of such factors as level of concentration, techniques used, sample heterogeneity, and contamination. While all these factors contributed in varying degrees, the ultimate conclusion was that some laboratories consistently performed better than others."

A contributing factor to the disparity in results of collaborative analysis of rock reference samples has been mentioned earlier in this paper – namely, the failure of some scientists to grasp the limitations of some of the newer forms of analytical instrumentation. It appears to matter little whether one is, say, a geologist or an experienced analytical chemist, but in going into a new instrumental technique, one must be wary not to take too literally the over-simplistic explanations of sales people. Such statements as "technique Z is quick and easy", or "technique X is simpler than technique Y" should be viewed with skepticism. Brunfelt and Steinnes (1978) stated the case indirectly but well: "Unfortunately the increased activity in NAA seems to have involved the reporting of an increasing number of data suffering from insufficient consideration of sources of systematic error". A less gentlemanly statement of the same state of affairs might be: "...increased activity in instrumental methods seems to have involved an increasing number of analysts who did not know what they were doing". Several "horrible" examples of the situation were cited by Abbey (1981b).

All of the above appears to confirm the proposition that inter-laboratory factors greatly outweigh sample inhomogeneity as the cause of disparate results. Sample inhomogeneity remains a serious problem, but generally where it does occur, it can be overcome with some special effort.

The select laboratories method was designed to use the existence of inter-laboratory factors in a constructive manner. Since its initial introduction (Abbey, 1970), the method has undergone many modifications (improvements, one hopes) but the essential principles remain the same:

a) All results for a given constituent in a given sample are classified as "good", "fair" or "poor" on the basis of their positions in the distribution.

b) Each contributing laboratory is given a rating, based on its relative numbers of good, fair and poor results.

c) Only the results reported by laboratories with ratings above a specified level are used in arriving at the desired value.

Changes in the method have concerned the elimination of far outliers; the manner in which the good, fair and poor results are identified; the decision as to what constitutes a separate laboratory; the level above which a laboratory may be considered to fall within the select group; the method of evaluating the final value from the group of select values; special treatment (or otherwise) for trace elements as distinct from major and minor constituents; and the handling of results for which the numbers available are insufficient to justify more elaborate treatment.

Evolution of the Method

Application of the method in a series of publications illustrates the various changes that have been incorporated and the reasons for them.

In the first case (Abbey, 1970), only the major and minor constituents were considered, although chromium, nickel, strontium and barium were also included (as oxides) – and chlorine as element – because they occurred at the 0.01 per cent level or higher in some of the samples under study – USGS II. The mean and standard deviation were computed for each constituent of sample G-2 and the results immediately showed that the distributions were far from normal – i.e. the fraction of the results within one standard deviation of the mean, far from being about 0.68, varied from 0.70 to 0.94. For the entire set of data on G-2, the ratio was 0.82. (Let us remember that G-2 is not an unusual sample and certainly falls within the "common granite" composition referred to by Schlecht (1951)).

The increased proportion of results falling within one standard deviation is easily understood as the result of the presence of outlying values. Such values cause a large increase in the standard deviation which then of course includes an increased number of results.

The rejection of about 32 per cent of the data – as would occur in a normal distribution where one standard deviation was the limit – would be considered excessive by many who are familiar with typical results in a collaborative program. The 18 per cent beyond one standard deviation, as with G-2, might be considered somewhat more realistic. To carry the reasoning somewhat further, it was decided to reject 15 per cent of the data before computing a "preferred mean" of the remainder. The values thus rejected were eventually labelled "poor" for purposes of calculating laboratory ratings.

In order to establish a criterion for dividing the remaining values into "fair" and "good", "numerical histograms" were plotted, two examples of which are given in Figures 1 and 2. Size of the class intervals was arbitrary, merely "the smallest possible, consistent with including extreme values, on a sheet of paper of convenient size".

It was decided that "good" results would be recognized as all of those falling within the same class interval as the "preferred mean", as well as those within the two immediately adjacent intervals. Thus, in Figure 1, where there are 45 results plotted, the "poor" values would be 0.15 X 45 = 6.75 (i.e. 7) in number. The overall mean being 67.21, the seven farthest removed from that mean – i.e. 64.69, 64.73, 65.0, 66.4, 68.05, 69.57 and 69.88 – would be considered "poor". The preferred mean (the mean of the results remaining after removal of the seven poor ones) is 67.26, which falls within the class interval 67.10 to 67.29, so inclusion of the immediately adjacent intervals would mean that the values 66.9 to 67.48 inclusive are considered "good". All values not designated as either "poor" or "good" would then be considered "fair". In Figure 1, the solid vertical lines represent the boundary between good and fair values; the broken lines, the boundary between fair and poor. Figure 2 shows the distribution for a constituent with more erratic results, with the boundaries having the same significance as in Figure 1.

As the good, fair and poor results were identified for each constituent of the six samples in USGS II, a running score of the number of results in all three categories was noted for each contributing laboratory. Designation of what

Figure 1

Numerical Histogram

SiO_2 in GSP-1

(per cent)

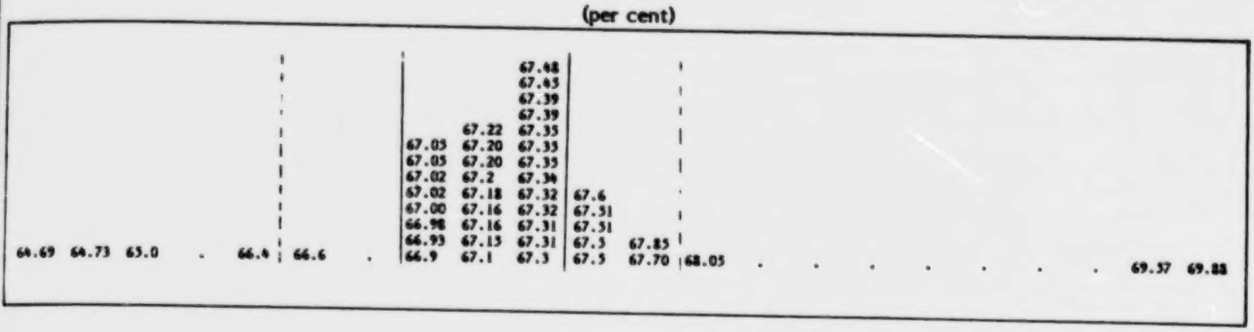
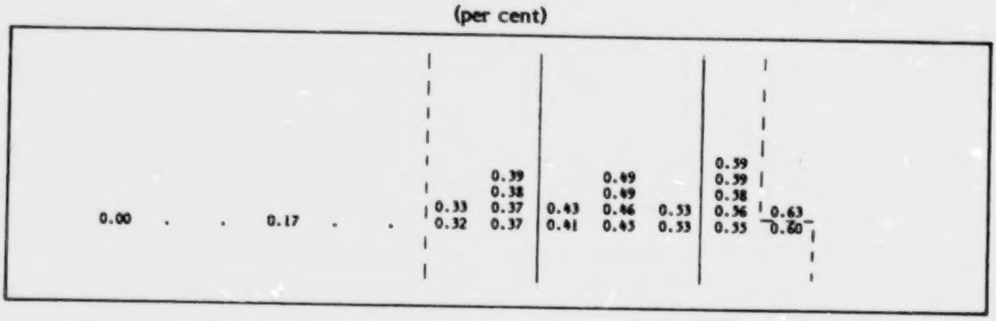


Figure 2

Numerical Histogram

H_2O^+ in DTS-1

(per cent)



constituted a "laboratory" was somewhat arbitrary. In general, each laboratory was identified by its institution – e.g. University of X, Y Research Institute, Geological Survey of Z, etc. However, in cases where there were pronounced differences in the quality of results from two or more reporting groups within the same institution, such groups were considered as separate laboratories. In that way, it was possible to make use of the results reported by the better groups instead of having their rating depressed by the less acceptable performance of other groups in the same organization.

The total number of good, fair and poor results was then substituted in the following formula (for each laboratory):

$$R = \frac{N_G - N_P}{N_G + N_F + N_P} \times 100,$$

where R is the laboratory rating,
N_G the total number of good results,
N_F the total number of fair results, and
N_P the total number of poor results.

A rating of 51 or better was taken as the requirement for qualification as a "select" laboratory. Only eight of the laboratories that had contributed a minimum of 40 results for the constituents under study qualified as "select". For each constituent of each sample, the mean of the results reported by the select laboratories was calculated. In general, those means were taken as "proposed values", although subjective considerations resulted in a few changes. Of the 106 values finally proposed, 99 were the means of results from the select laboratories ("select means"), three were from the calculated "preferred means" and four were based on more purely subjective considerations.

The next undertaking (Abbey, 1972) involved a compilation of analytical data of 18 reference materials, from various sources, which were considered suitable for use as calibration standards in the general analysis of silicate rocks. A limited number of values were also listed for several less established samples. The six samples of USGS II were included, using the values derived earlier (Abbey, 1970), except for small corrections in the barium contents of BCR-1 and GSP-1. That time, however, values were also assigned to a number of trace elements. Using Flanagan's (1969) compilation, plus additional data appearing in later literature, values were assigned which were the means of remaining values after rejecting the 20 per cent of the original values that were farthest removed from the overall mean.

For the French samples, the values recommended or proposed by the originators (Roubault et al., 1968) were used. Originators' values were also used for samples issued by the U.S. National Bureau of Standards and the British Bureau of Analysed Samples. For several other samples where there were insufficient data to justify use of the select laboratories method, values for major, minor and a few trace elements were derived by a procedure essentially the same as that described above for trace elements in USGS samples.

Thus, in terms of the evolution of the select laboratories method, the paper under discussion (Abbey, 1972) merely involved the use of what came later to be known as the "abridged method", consisting essentially of a variant of the idea of a trimmed mean. Two other ideas were introduced at that point – the term "usable value" and the use of the question mark. "Usable value" is intended to imply, as the term suggests, that the value may be used – but with more caution than those described by others with such more assertive terms as "best", "recommended", "accepted", "certified", "guaranteed", etc. Use of the question mark implies a relatively greater degree of uncertainty – a subject covered in more detail in the section on "uncertainty limits".

In the next paper in the series "Studies in 'Standard Samples'..." (Abbey, 1973), there was no significant change in the select laboratories method, but an effort was made at clarification of the use of the question mark. For major and minor elements for which there were insufficient data for the more elaborate method – and also for all trace elements – the question mark identified values based on the mean of fewer than 10, but more than four results. It was also used to indicate increased uncertainty for other reasons – generally of a subjective nature. No values were assigned for components for which fewer than five results were available.

All values reported in that paper (Abbey, 1973) had been converted to the dry basis, in order to reduce all values to the same, theoretically reproducible state. Unfortunately, that operation introduced potential errors, because consensus values (of one kind or another) of H_2O^- concentrations were used to convert values to the dry basis. In the ideal case, where all contributors report H_2O^- results with all their other data, or report all data on the dry basis, it is not difficult to reduce all results to the common state. Unfortunately, very few analysts involved in collaborative programs actually report H_2O^- values; a few others report on the dry basis; the majority tend to ignore the difference between "as received" and "as dried". For many rocks with H_2O^- contents under 0.1 per cent, the difference between the two states is relatively insignificant. Where H_2O^- exceeds one per cent, significant errors may be introduced. In such cases, there is really no way to eliminate the potential errors because the available data are inadequate. In later work, this writer based all calculations on the assumption (unfortunately not a good one but possibly the least of several possible evils) that all data reported without H_2O^- values are to be considered as being on the dry basis.

In the next compilation (Abbey, 1975b), three minor modifications were introduced:

i) The "preferred mean" was defined as the mean of remaining values after eliminating the 20 per cent of the available values that were farthest removed from the overall mean.

ii) The values eliminated in (i) were designated as "poor", instead of those representing 15 per cent of the available values. (This change had an almost imperceptible effect on the final results.)

iii) After establishment of "select values", provision was made for the elimination of outliers among those values that differed from their nearest neighbor by as much as or more than the latter differed from the opposite extreme, before calculating the "select mean". (Some subjective judgment was also injected in the use of this provision).

Several additional changes were introduced in the compilation that followed (Abbey, 1977b):

i) The test for the elimination of extreme outliers was applied both to the original raw data before beginning any other calculations (such values being included among the "poor"), and to the select values before calculating their mean.

ii) For constituents where only five to nine results were available, their median was taken as the usable value, but the resulting uncertainty was indicated with a question mark.

iii) For constituents where only three or four results were available, provided that those results were in close agreement, were reported by at least three different laboratories and based on at least three different methods, the median was used, with a question mark, as in the preceding case. (Considerable selective judgment was involved in such cases).

iv) The rating level setting the limit between select laboratories and others was made flexible but set at a particular point in working with a particular group of samples. This change was necessary to adapt to situations where, as a result of limited available data or of major imbalance in the quantity of data reported by the various laboratories, it was not possible to derive a reasonable number of select values. (Again, subjective judgment played a significant rôle in setting the "selectivity limit").

v) Trace elements were treated in the same manner as were major and minor constituents.

Up to this point, emphasis has been placed on the advantages of the select laboratories method relative to other proposals for evaluating compositions from highly scattered data. No mention has been made of the drawbacks of the "select" approach, the most serious being the tedious and time-consuming aspect. Attempts to simplify things by use of a mini-computer proved difficult, partly because some of the concepts involved could not be readily expressed in a numerical manner.

A major change was introduced in the method of classifying results as good, fair and poor, in the course of re-evaluating the USGS II samples (Abbey, 1978). The mean and standard deviation of all results (after rejecting extreme outliers, as defined above) were calculated. All results beyond one standard deviation of the mean were classified as "poor", and set aside. A new mean (the "preferred mean") and standard deviation of the remainder were then calculated. All results beyond one standard deviation of that mean were categorized as "fair", and set aside. The results in the second remainder were regarded as "good". These changes permitted the subsequent adaptation of a programmable calculator to the first stages of the computations of the method, and later, to the use of a computer program.

Additional changes in the same paper were:

i) In all cases where there were insufficient results to justify use of the full method, the median of available results was taken as usable value, but reported with a question mark.

ii) Both mean and median of the select values were calculated and a subjective choice made between them on the basis of the summation and iron-oxide compatibility tests. Where doubt existed, the median was favoured.

An attempt was made to provide a somewhat finer resolution of the degree of reliability of derived values in a summary report on the three Canadian rocks, SY-2, SY-3 and MRG-1 (Abbey, 1979). The category "A" was assigned to constituents for which at least 20 results had been reported, where there was no apparent bias in their distribution and where there was close agreement between median, mean, mode, select median and select mean. (Again, some degree of subjectivity was involved). The question mark was used as outlined above. Results falling between the two extremes were given as "B".

The "A" and "B" categories were not included in the next major compilation (Abbey, 1980) because the necessary information was not available for all of the samples listed. One significant change involved application of the select laboratories method to two programs, each of which involved only one sample. In those cases, only trimmed means had been used previously because of the limited amount of available data, but it was found that the select laboratories method produced results with improved summations and iron-oxide compatibility.

Continuing modification of the details of the select laboratories method may be regarded as a weakness; this writer prefers to consider it a strength, in that it permits adjustment to differing circumstances as well as an opportunity to profit from past experience.

Various colleagues have questioned the validity of the "closed-circuit thinking" that appears to occur in such adjustments. Still, the various "tests of validity" of derived values, as illustrated in several tables in this report, clearly indicate the apparent superiority of values derived by the select laboratories method. A case in point concerns the subjective choice between the median and the mean of the results reported by the select laboratories. Tests have shown that either one of those measures generally produces values superior to those derived by the methods using the various trimmed means, medians, modes, etc. The final choice merely serves to put the final edge on what is apparently already a sharp tool.

The most recent modification was brought about as a result of gross imbalance in the numbers of results reported by various laboratories on samples designated as USGS III (Abbey, 1982a). A half dozen of the 50 laboratories involved had reported nearly half of the results, and the total number of results was much smaller than those reported in most other programs. Problems arose in deciding on a rating level above which laboratories would be considered "select". For example, one laboratory had reported 359 results – more than any other – of a total of 2733, and had a rating of 36.5. If 40 were taken as the minimum rating to qualify as "select", the data from that laboratory would have been excluded. The limited select values (884 out of 2733) would have severely restricted the number of constituents for which unquestioned usable values could be derived. If the limit were set at 30 – or even at 35 – it was found that the concept of selectivity was largely lost; for some constituents, as many as 10 select values were found out of only 12 reported by all sources. The situation was partially due to the fact that several different methods were used for a number of constituents by the laboratory with the largest number of results.

An additional set of rules was adopted to minimize these difficulties. As a first step, the lower limit of rating for eligibility as a select laboratory was set at a point where more than one third but less than one half of the total number of reported results would fall within the select group. For each individual constituent, the cut-off level was raised or lowered in order that the select values be at least five, but no more than half the results reported for that constituent, provided that the limits specified in the first step are observed.

These last changes injected additional subjectivity into the method. It may be that few, if any, future programs would involve so few results and such gross imbalance; these last steps may then be unnecessary.

Table 3 shows a comparison of derived values for USGS II, based on the earliest version of the select laboratories method (Abbey, 1970, 1972) and on a more recent version (Abbey, 1978). The values derived by the earlier version have been converted to the dry basis, using the then derived values of H_2O^-. Flanagan's (1976c) recommended, average and magnitude values are also shown, again converted to the dry basis, using his "best values" for H_2O^-. It should be noted, however, that the values from Abbey (1970, 1972) were based only on Flanagan's first compilation (1969), whereas those from Abbey (1978) and Flanagan (1976c) included results from both Flanagan compilations (1969, 1976c). In Table 3, only those constituents for which values were available from all three sources are included.

In Table 4 the summation and iron-oxide compatibility tests are applied to the values in Table 3. In comparing the original with the later version of the select laboratories method, it can be seen that the summation in five of the six samples is closer to 100 per cent in the recent version. Similarly, the iron-oxide compatibility is improved in four of six cases. Flanagan's values do not compare favourably.

The above evidence tends to support the view that the modifications embodied in the select laboratories method over recent years have resulted in appreciable improvement. How that method compares with others is described in a later section of this paper.

UNCERTAINTY LIMITS

It cannot be denied that a "usable value" for the concentration of a constituent in a reference material would be more meaningful if a quantitative measurement of the degree of uncertainty (to some specified level of confidence) were included. In practice, such limits are not easily assigned. Sutarno and Fay (1975) based their 95 per cent confidence limits on a rigorous statistical scheme which takes into account within- and between-bottle variances and other variables in a multiple-sampling scheme which also deduces a parameter (the "certification factor") to indicate whether a given value is "certifiable". Christie and Alfsen (1977), took the standard deviation of their transformed data and back-transformed it to give asymmetrical limits on their Gamma Central Value.

A minor question can arise in connection with the work of Christie and Alfsen. They referred to their limits as "68 per-cent confidence", presumably on the assumption that their transformed data were normally distributed. In fact, their transformation function serves merely to reduce skewness, with no regard to kurtosis, which can significantly affect the fraction of the data points that lie within one standard deviation.

Gladney (1980, 1981) and Gladney and Goode (1981) gave the standard deviation of the mean of remaining values (after deleting outliers) as their measure of uncertainty.

As is the case with reported data in everyday analyses, one wonders how meaningful such "plus-or-minus" figures can be. Very often, it appears that they represent no more than the variability of readings on the instrument used for final measurement.

Table 3. A Comparison of values for USGS II

	AGV-1			BCR-1			DTS-1		
Pct	1*	2*	3*	1	2	3	1	2	3
SiO_2	59.69	59.61	59.61R	54.85	54.53	54.94R	40.68	40.61	40.52R
TiO_2	1.07	1.06	1.05R	2.26	2.26	2.22R	0.01?	0.00?	0.013?
Al_2O_3	17.22	17.19	17.43	13.68	13.72	13.72R	0.29	0.25	0.24
Fe_2O_3	4.44	4.56	4.56R	3.48	3.48	3.72R	0.85?	1.02?	1.21R
FeO	2.04	2.03	2.07R	9.05	8.96	8.87	6.98?	6.94?	7.23
MnO	0.10	0.10	0.098	0.19	0.18	0.18R	0.13	0.12	0.11R
MgO	1.55	1.52	1.53	3.49	3.48	3.49R	49.80	49.80	49.83R
CaO	5.00	4.94	4.95	7.00	6.97	6.98R	0.14?	0.14	0.15R
Na_2O	4.31	4.32	4.30R	3.29	3.30	3.30R	0.01?	0.01?	0.007R
K_2O	2.90	2.92	2.92R	1.68	1.70	1.71R	0.00	0.00	0.0012R
H_2O^+	0.61	0.78	0.82R	0.73	0.67	0.78R	0.41	0.42	0.46R
CO_2	0.01	0.02	0.05?	0.02	0.02	0.03?	0.06	0.07	0.08?
P_2O_5	0.50	0.51	0.50R	0.33	0.36	0.36R	0.00?	0.00?	0.002?
F	0.04	0.04	0.044	0.05	0.05	0.047?	0.00?	0.00?	0.00?
S	0.01?	0.01?	<0.001	0.04?	0.04?	0.039?	0.00?	0.00?	0.00?
PPM									
Ag				30?†	35?†	36?†			
Ba	1220	1200	1208R	710	680	675R			
Ce	70?	71	63	50?	53	53.9R			
Co	17	16	14.1	50	36	38?	135	135	133
Cr	12	10	12.2	16	15	17.6	4400	4200	4000
Cs	1.3?	1.3?	1.4?	1.0?	0.95?	0.95R			
Cu	63	59	59.7	19	16	18.4	7	5	7.0
Dy				6.7?	7?	6.3R			
Eu				2.0?	2.0?	1.94R			
Ga	20	19	20.5R	23	22	20?			
Ge				1.5?	1.5	1.54			
Hf	5?	5?	5.2	4.5?	5	4.7			
La	45?	36	35?	25	27	26?			
Li	14	12	12	15	14	12.8R			
Lu	0.35?	0.3?	0.28	0.6?	0.5?	0.55R			
Mo	3?	3?	2.3?	3?	1.5?	1.1?			
Nb	18?	16?	15R	17?	19?	13.5R			
Ni	17	15	18.5	13	10	15.8	2400	2300	2269
Pb	36	33	35.1	15	14	17.6	11	11	14.2
Rb	70	67	67R	50	47	46.6R			
Sb	4.3?	4.3?	4.5	0.6	0.6	0.69	0.6?	0.5?	0.46?
Sc	12	12.5	13.4	34	33	33?	4?	3.8	3.6?
Sn	5?	3.6	4.2	4?	2.5	2.6?	2.3?	1.7?	1?
Sr	670	660	657R	330	330	330R			
Ta	0.8?	1.4?	0.9R	0.8?	0.8?	0.91R			
Tb	0.7?	0.7?	0.70R	1.0?	1.0?	1.0R			
Th	7	6.4	6.41R	7	6.1	6.0R			
Tl				0.14?	0.3?	0.3			
U	2.0	1.95	1.88	1.8	1.7	1.74	4?†	4?†	4?†
V	125	125	125	410	420	399	13	11	10.3
Y	26	19	21.3	46	40	37.1			
Yb	2.0	1.9	1.7	3.8	3.4	3.36			
Zn	88	86	84R	120	125	120R	47	46	45R
Zr	220	230	225R	185	185	190?			

	G-2			GSP-1			PCC-1		
Pct	1	2	3	1	2	3	1	2	3
SiO_2	69.30	69.22	69.19R	67.31	67.32	67.46R	42.15	42.10	42.11R
TiO_2	0.48	0.48	0.50R	0.65	0.66	0.66R	0.01	0.01	0.015?
Al_2O_3	15.35	15.40	15.42	15.19	15.28	15.27R	0.73	0.73	0.74
Fe_2O_3	1.01	1.07	1.08R	1.60	1.70	1.77R	2.50?	2.54?	2.86R
FeO	1.45	1.44	1.45R	2.34	2.32	2.31R	5.17?	5.17?	5.27
MnO	0.04	0.03	0.034	0.04	0.04	0.043	0.12	0.12	0.12R
MgO	0.77	0.75	0.76	0.98	0.97	0.96R	43.63	43.50	43.40
CaO	1.98	1.96	1.94	2.06	2.03	2.02R	0.53	0.55	0.51
Na_2O	4.06	4.06	4.07	2.77	2.81	2.80R	0.01	0.01	0.006?
K_2O	4.50	4.46	4.51R	5.50	5.51	5.54R	0.00	0.00	0.004?
H_2O^+	0.48	0.50	0.55R	0.54	0.58	0.57R	4.64	4.70	4.72R
CO_2	0.08?	0.08?	0.08?	0.12	0.12	0.15?	0.16	0.18	0.12?
P_2O_5	0.14	0.13	0.14R	0.28	0.28	0.28R	0.00	0.01	0.002?
F	0.13	0.12	0.129?	0.38	0.37	0.32?	0.00?	0.00?	0.002?
S	0.01?	0.01?	0.002?	0.04?	0.03?	0.016?	0.01?	0.01?	<0.001?
PPM									
Ba	1840	1900	1870R	1335	1300	1300R			
Be	2.6	2.4	2.6	1.5?	1?	1.5?			
Ce	150?	160	150?	440?	360	394			
Co	6	5	5.5	7	7.8	6.4	110	110	112
Cr	9	8	7?	13	12	12.5	3000	2800	2730
Cs	1.3	1.4	1.4?	1.0	1	1.0R			
Cu	11	10	11.7	35	33	33.3	11	8	11.3
Ga	22	23	22.9R	21	23	22?			
Hf	7.5?	8?	7.35	13?	14?	15.9			
La	100	92	96	205	195	191			
Li	37	35	34.8	34	30	32.1			
Lu	0.15?	0.2?	0.23						
Mo	1.5?	0.9?	0.36?	2?	1.5?	0.90			
Nb	11?	13?	13.5R	27?	23?	29R			
Ni	6	3.5	5.1	9	9	12.5	2500	2400	2339
Pb	29	30	31.2	53	54	51.3	10	11	13.3
Rb	170	170	168R	260	250	254R	1?	0.3?	0.063
Sb	0.1?	0.06?	0.1?	3.0?	3.1?	3.1			
Sc	4	3.5	3.7	8	6.6	7.1	9?	9?	6.9
Sn	1.9?	1.4?	1.5?	8?	5?	6.3	2.5?	1.6?	1?
Sr	480	480	479R	250	240	233R	1	0.4	0.41R
Ta	0.8	0.8	0.91R						
Tb	0.5?	0.5?	0.54R	1.3?	1.4?	1.3R			
Th	25	25	24.2R	110	105	104R			
U	2.0	2.1	2.0	2.0	2.1	1.96	3?†	5?†	5?†
V	34	36	35.4	49	54	52.9	31	29	30
Y	12	11	12R	32	29	30.4			
Yb	0.9	0.86	0.88	2.5	1.9	1.8			
Zn	85	84	85R	105	105	98R	44	41	36R
Zr	310	300	300R	560	500	500R			

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† - PPB

* - 1: Abbey (1970, 1972). Original select laboratories method, values converted to dry basis.

2: Abbey (1978). Revised select laboratories method, values on dry basis

3: Flanagan (1976c). R: recommended; ?: magnitude; others "averages", all values converted to dry basis.

Table 4. Summations and iron-oxide compatibilities for USGS II

	AGV-1			BCR-1			DTS-1		
	1	2	3	1	2	3	1	2	3
Sum*	99.75?	99.81?	100.25?	100.36?	99.95?	100.61?	100.33?	100.31?	100.75?
Fe_2O_3TR	6.81	6.78	6.83R	13.52	13.41	13.51R	8.60	8.70	8.64R
Fe_2O_3TC	6.71	6.82	6.86R	13.54	13.44	13.58	8.61?	8.73?	9.24

	G-2			GSP-1			PCC-1		
	1	2	3	1	2	3	1	2	3
Sum	100.10?	100.06?	100.21?	100.02?	100.26?	100.45	100.44?	100.38?	100.34?
Fe_2O_3TR	2.67	2.69	2.65	4.26	4.30	4.33R	8.28	8.28	8.39
Fe_2O_3TC	2.62	2.67	2.69R	4.20	4.28	4.34R	8.25?	8.29?	8.72

* Sum includes trace-element equivalents and correction for Cl, F, S.

1, 2, 3 - as in Table 3

Fe_2O_3TR - derived value for total iron, expressed as Fe_2O_3.

Fe_2O_3TC - calculated value for total iron, expressed as Fe_2O_3, from derived values of Fe_2O_3, and FeO.

It is interesting to note that the systems cited above for assigning uncertainties or confidence limits involved workers who are not involved in the preparation, analysis and evaluation of rock reference samples. All have been involved in one or two of those steps, but not in all three. By contrast, those who have been responsible for all three steps for rock samples (e.g. Flanagan, 1969, 1976c; Steele et al., 1978; Steele and Hansen, 1979; Ando et al., 1974; Govindaraju, 1980) have not, at this point, assigned such limits to their "recommended" or "consensus" values. May we assume that their reluctance is the result of tacit assumption that some of the factors in the distribution of results are not quantifiable?

If such be the case, it accords with the principles underlying the select laboratories method – i.e. that the spread of values reported are not due mainly to random analytical error, but to systematic inaccuracies, often the result of insufficient understanding of analytical principles. In those circumstances, it can be argued that the standard deviation (or multiples thereof) – or any other statistical property of the distribution – is not a realistic reflection of the uncertainty of the finally assigned value.

On the other hand, in the course of arriving at the relatively small group of results emanating from the better sources, as in the select laboratories method, one has presumably significantly reduced the systematic error component of the distribution. Statistical properties of these "select results" might then give a truer picture of the uncertainty of a derived value.

In the select laboratories method, the usable value may be the mean, or more often the median of the select results. Where the mean is used, one standard deviation might be appropriate – ca 68 per cent confidence (assuming the distribution to be more nearly normal than is that of the entire set of raw data) or two standard deviations for ca 95 per cent confidence under the same assumptions. Dixon and Massey (1957, p.294, 462) presented a method for determining the 95 per cent confidence limits of the median. In both cases (mean or median), with the relatively small number of data points among the select results (say, up to eight), the 95 per cent confidence limits are, in effect, the entire range of the select results.

In the first application of the above reasoning (Abbey, 1982a), the results of application of the select laboratories method were being compared with those of Gladney and Goode (1981). Since those authors had used one standard deviation as the measure of uncertainty, it was necessary to use a "68 per cent analog" of the uncertainty where the median of the select results was chosen as usable value. That was achieved by taking half the difference between the median and the highest of the select results as "positive uncertainty", with a corresponding negative uncertainty equal to half the difference between the median and the lowest of the select results. The overall result was a marked reduction in the magnitude of the uncertainties when compared to those of Gladney and Goode (1981). A certain degree of unfairness must be admitted in the foregoing comparison, because nearly twice as many raw results were available to Abbey (1982a) than there were to Gladney and Goode. Nonetheless, the comparison does make a plausible case for the assumption that the statistical properties of a

Table 5. A comparison of 16 estimates of "best value" (all figures in per cent)

	SY-2			SY-3			MRG-1		
	Sum	Fe_2O_3TR	Fe_2O_3TC	Sum	Fe_2O_3TR	Fe_2O_3TC	Sum	Fe_2O_3TR	Fe_2O_3TC
M	100.34	6.32	6.44	100.49	6.51	6.53	100.50	17.98	18.14
$\bar{X}$	100.42	6.39	6.46	100.71	6.53	6.62	100.52	17.99	18.05
$\bar{X}_C$	100.43	6.35	6.42	100.56	6.51	6.55	100.41	18.02	18.05
$\bar{X}_B$	100.30	6.36	6.44	100.62	6.49	6.57	100.36	17.97	18.06
$\bar{X}_1$	100.32	6.34	6.46	100.56	6.49	6.57	100.35	17.98	18.03
$\bar{X}_2$	100.33	6.32	6.46	100.48	6.48	6.54	100.46	17.97	18.12
GM	100.22	6.38	6.43	100.59	6.55	6.51	100.36	18.03	17.98
DCM	100.08	6.31	6.39	100.30	6.52	6.41	100.71	17.93	18.19
MHM	100.15	6.25	6.38	100.20	6.36	6.45	100.71	17.82	18.23
GTM	100.26	6.36	6.45	100.59	6.55	6.51	100.44	18.02	18.08
MHTM	100.34	6.33	6.40	100.33	6.51	6.53	99.94	18.01	18.18
PMM	99.95	6.35	6.35	100.18	6.35	6.51	100.60	17.90	18.20
X_i	100.47	6.31	6.38	100.74	6.51	6.49	100.27	18.02	17.71
M_s	100.17	6.26	6.30	100.20	6.41	6.44	100.37	17.79	17.95
$\bar{X}_s$	100.23	6.28	6.33	100.33	6.42	6.42	100.18	17.82	17.85
V_u	100.13?	6.28	6.30	100.17?	6.42	6.42	100.14?	17.82	17.85

M = the median of all results for each constituent;
$\bar{X}$ = the arithmetic mean of all results for each constituent;
$\bar{X}_C$ = the mean of remaining results after deletion of all beyond three standard deviations of $\bar{X}$
$\bar{X}_B$ = the mean of remaining results after deletion of all beyond two standard deviations of $\bar{X}$
$\bar{X}_1$ = the mean after deletion of results beyond one standard deviation of $\bar{X}$
$\bar{X}_2$ = the mean after deletion of results beyond one standard deviation of $\bar{X}_1$
GM = the geometric mean of all results for each constituent (Sankar Das, 1979);
DCM = the dominant cluster mode of all results for each constituent (Ellis et al., 1977);
MHM = the moving histogram mode (Abbey et al., 1979);
GTM = the Gamma transformation mode, or Gamma central value (Christie and Alfsen, 1977).
MHTM = the moving histogram transformation mode (Abbey et al., 1979);
PMM = the plot method mode (Colombo, 1980b, as modified by Abbey, 1981a);
X_i = the "Ingamells value" (Ingamells, 1978, as slightly modified by Abbey, 1981a);
M_s = the median of results reported by "select laboratories" (Abbey, 1980);
$\bar{X}_s$ = the mean of results reported by "select laboratories" (Abbey, 1980);
V_u = the "usable value", chosen subjectively from M_s and $\bar{X}_s$

smaller, select group of data which presumably incorporates a reduced proportion of results involving systematic error, give a more realistic estimate of the uncertainty of the assigned values than would similar properties of all the raw data. Unfortunately, as is the case with the select laboratories method as a whole, much evidence can be brought forward to support the foregoing assumptions, but rigorous proof is another matter. On the other hand, the very fact that so many other methods have been proposed for resolving disparate data, all presumably based on sound statistical reasoning, strongly suggests that rigorous proof of the validity of any of them is not likely to be forthcoming.

COMPARISONS

Several cases have been cited above to support the claim of superiority of the select laboratories method of resolving disparate data. Thus in Table 2, results of that method are compared with those of Gladney (1981), which are based essentially on trimmed means; in Table 4, results by both earlier and later versions of the method are compared with those of Flanagan (1976c), the exact nature of whose method has never been made clear.

In the course of introducing the moving histogram mode and moving histogram transformation mode, Abbey et al. (1979) used the iron-oxide compatibility test on data for 10 different reference rocks to compare the performance of 13 different approaches to a "best value" for the different iron oxides. Results tended to favor the select laboratories method, but there were some reservations because the study concerned only the iron oxides.

Abbey et al. (1979) also stated: "Ideally the best overall test for each estimate would involve 'complete' analysis of a group of samples [by a number of laboratories], computation of the various estimates and subjection of each of the results of those computations to the summation test, the iron-oxide compatibility test and the comparative analytical test" – the last of these was proposed in Abbey (1977a). An opportunity for just such a comparison became available in a re-evaluation of three Canadian rocks (Abbey, 1981a). Table 5 compares the performance of 16 different estimates of best value, using the summation and the iron-oxide compatibility test.

The "Sums" shown in Table 5 include all trace elements present at levels sufficiently high to affect the summation; they have also been corrected for the oxygen equivalents of fluorine, chlorine and sulphur. Fe_2O_3TR and Fe_2O_3TC have been explained earlier in this paper; both represent total iron, expressed as ferric oxide, the former being based on reported values for total iron, the latter on reported values for ferric and ferrous.

In Table 5, the different measures of best value are subjected to two different tests on three different samples, i.e. each measure is subjected, in effect, to six tests. The "usable value", V_u, subjectively derived from M_s and $\overline{X}_s$, gives the best performance on both tests for SY-3. For SY-2, PMM appears superior on both tests, but does poorly on both tests for MRG-1 and on the iron-oxide test for SY-3. MHTM appears superior to V_u in the summation for MRG-1, and is close to the performance of V_u on the iron oxides for SY-3, but does relatively poorly on all other tests. Similarly, $\overline{X}_c$ matches the iron-oxide compatibility of V_u for MRG-1, but is unimpressive in all other tests. In those cases where V_u does not produce the best results (both tests for SY-2, summation for MRG-1), it is never worse than second-best.

In view of the involved procedure used in deriving V_u, an attempt was made to find which simpler process, if any, could be used to attain values reasonably close to V_u. Table 5 gives no indication that any other measure comes close – with the possible exceptions of M_s and $\overline{X}_s$, but those are the ones upon which V_u is based. A search for the measure whose values for each constituent differed least from V_u revealed a highly erratic pattern, varying from one sample to another and also differing between major, minor and trace constituents.

We come now to an example of the "comparative analytical test" (Abbey, 1977a). That test was proposed as follows: "...given a set of, say, at least four reference samples, the assigned concentration values for a particular element in the different samples can be compared to one another by taking all of the samples through a reliable analytical method, and plotting the final signal [where a linear relationship exists between concentration and signal]... against the assigned concentration values. If the plotted points are sufficiently close to a straight line, the correctness of the assigned values for the same element in the different samples would be confirmed, at least relative to one another. All may still be subject to a consistent bias. However, the likelihood of such bias becomes less as the number of samples involved becomes greater, particularly if the samples are of variable overall composition, if they originated in different collaborative programs, and if more than one analytical method were used in the verification test".

Belyaev and Sobornov (1981) measured potassium, uranium and thorium in 43 reference samples, originating in the USSR, East Germany, Austria, Japan, USA, and Canada, by means of gamma ray spectroscopy. For calibration, they used 13 of the same group, three from the USA, one from Japan, two from Canada, two from East Germany and five from the USSR. They quoted Abbey (1980) in listing the calibration standards, presumable implying that they used the values for the elements concerned as listed in that publication, although they included two samples that were not listed there. From the resulting straight-line calibrations, they determined the potassium, uranium and thorium contents of the other 30 samples, also reading off what amounted to regression values for the 13 used for calibration.

Of the 43 samples, there are 16 where it is possible to compare the results of Belyaev and Sobornov with the values listed in Abbey (1980) for one or more of the three elements. There are eight others where the results may be compared to those listed in Abbey (1982a). Of the 24 samples for which such comparisons can be made, 15 have values based on the select laboratories method, namely BCR-1, MRG-1, AGV-1, GSP-1, G-2, SY-2, SY-3 (Abbey, 1980) and BHVO-1, RGM-1, QLO-1, STM-1, MAG-1, SGR-1, SCo-1, SDC-1 (Abbey, 1982a). Values for the nine others are based on other derivation methods. Belyaev and Sobornov reported all of their results with plus-or-minus uncertainties. In the comparisons listed in Table 6, only values without question marks (Abbey, 1980, 1982a) were used.

The numbers quoted in Table 6 refer to values for individual elements (i.e. one, two or three per sample). The following points are noteworthy:

a) The 15 "select laboratories" samples contributed only 12 calibration points; the nine "other methods" samples gave 14 such points. One might therefore expect the calibration curve to be somewhat favourable to the latter group.

b) Of the 24 possible comparisons with the former group, only one third gave results whose uncertainty range did not embrace the published recommended values; fully 72 per cent of the 18 possible comparisons possible with the latter group failed to encompass the recommended values.

Table 6. Select laboratories method vs others (data of Belyaev and Sobornov (1981))

Samples with values derived by select laboratories method:	Used for calibration	Total comparisons	Outside limits	Per cent outside limits
(BHVO-1, BCR-1,MRG-1, AGV-1, GSP-1, RGM-1, G-2, QLO-1, SY-2, SY-3, STM-1, MAG-1, SGR-1, SCO-1, SDC-1)	12	24	8	33
Samples with values derived by other methods				
(BM, JB-1, ST-1A, SGD-1A, JG-1, GM, SG-1A, GnA, TB)	14	18	13	72

Belyaev and Sobornov (1981) concluded that some published recommended values should be changed, a conclusion which is justifiable. On the other hand, it is difficult to accept their next step, namely that the values found in their work should now be considered correct. Such a conclusion can be justified, perhaps, if there is absolute certainty that there is no systematic error in their method. Realistically, more confidence could be placed in their conclusion if their results were confirmed by means of an entirely different method, preferably in another laboratory. More importantly, however, Belyaev and Sobornov apparently did not notice the contradictions indicated in (a) and (b) above. Although they did not have access to the values in Abbey (1982a), they not only had access to those in Abbey (1980) but apparently used some of them for calibration.

Of the nine samples whose published values were derived by means of other than the selective laboratories method, JB-1 and JG-1 were from the Geological Survey of Japan, the others from the Zentrales Geologisches Institut, East Berlin, and the Institute of Geochemistry, Irkutsk. Potassium, uranium and thorium values for JB-1 and JG-1 in Abbey (1980) were based on Ando (1975) and Ando et al. (1975), who reported that most of their "estimated values" were based on the arithmetic mean of reported results; a few were taken from specially favoured analytical methods, such as isotopic dilution mass spectrometry and neutron activation.

The values for the East German samples are those given by Grassmann (1972), by Schindler (1972), and in the certificates provided with some of the samples. The values for the samples from Irkutsk are those of Tauson et al. (1974). The East German values were listed as "averages"; Tauson et al. merely stated that the values were calculated by means of a special computer program. In neither case was there any information on individually reported results. Dempir (1978) reported on the scheme used at the Geological Survey of Czechoslovakia and the Institute of Mineral Raw Materials to evaluate proposed reference materials. It appeared to depend heavily on arithmetic means, presumably after the rejection of extreme outliers. It is known that the two Czechoslovak institutions are closely associated with a co-ordinating body on geological reference materials, which includes institutions in most of the Eastern European "Comecon" nations (Valcha, personal communication, 1976). It may therefore be assumed with some confidence that the methods used for deriving recommended values from collaborative analytical data are much the same for all of the institutions involved; i.e. it is very likely that the values published by Tauson et al. (1974) for the Irkutsk samples were based on arithmetic means, after rejection of outliers, if any.

Abbey and Govindaraju (1978) reported results on those Irkutsk samples, as obtained in their respective laboratories. They stated: "The 1974 report in Russian on the three IGI samples has been translated by one of us (S.A.); pending permission to publish the translated version, we have decided to release the data contributed by GSC and CRPG in this journal."

As a result of the all-too-familiar communication problems with Eastern European countries, the permission to publish was never received. However, a translator's note appended to that unpublished document pointed out that if all "attested" values reported by Tauson et al. were summed, including trace elements, the resulting totals after O/F, S, Cl corrections were 100.32 for ST-1A, 100.40 for SGD-1A and 100.30 for SG-1A. Such slightly high summations are not uncommon, but they usually occur mainly with ultrabasic rocks. The translator then continued with: "The fact that the bias is of a similar magnitude and in the same direction for all three samples suggests that it is not due to random errors in the various recommended values, but that some systematic error may exist in the method of deriving the recommended values from the raw data. Unfortunately, no raw data are listed."

Readers who have managed to follow all of the foregoing tortuous reasoning may now observe that the figures in Table 6 serve to support the argument of the immediately preceding quotation. It follows that the apparently high scatter of the East German, Soviet and Japanese samples, relative to the Belyaev and Sobornov calibration line, provides yet another bit of evidence, if not in favour of the validity of the select laboratories method, at least against the assumption that mere elimination of outliers will leave a residue whose arithmetic mean will necessarily be the best approximation of the "true" value.

PART II

AVAILABLE MATERIALS

GENERAL

A preliminary, incomplete list appeared early in this paper when mention was made of some rock reference samples in the "historical review" of the subject. In any attempt at a more comprehensive listing, it becomes difficult to decide just which materials should be included. There are a number of citations in the literature which suggest possible sources for supply of reference samples (Flanagan and Gwyn, 1967; Flanagan, 1970, 1973; Abbey, 1972, 1973, 1975b, 1977b, 1980) for analysis of rocks and rock-like materials. Some citations are seriously in error, particularly regarding the difficult problem of calibration standards for trace-element determinations.

For example, Morrison (1975), in a report on "Methods of Calibration in Trace Analysis", recommended a set of synthetic glass wafers,"....doped with 61 elements at the 1-p.p.m. [SRM 614/615] and 0.2-p.p.m. [SRM 616/617] level .....for calibrating multi-element trace methods involving emission spectroscopy, spark source mass spectrometry, neutron activation analysis and X-ray fluorescence". In a table of "Sources of Standards", Morrison listed, among others, the Canadian Association for Applied Spectroscopy, the Geological Institute of Bulgaria, the Geological Survey of Tanzania, and the Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

In fact, the NBS wafers were at four levels, with intended trace-element contents of 500, 50, 1 and 0.02 (not 0.2) ppm. Of the two levels cited by Morrison, firm values (some of which differed greatly from the intended 1-ppm level) are listed for only 11 elements in SRM 614/615, according to the National Bureau of Standards (1979). For SRM 616/617, firm values are listed for only seven elements. Further, the fact that the samples are supplied as small wafers, one or three millimetres in thickness, and in small quantities of two or six, means that they can be used, in effect, only in nondestructive analytical systems which can utilize samples in that form. Thus the limited number of certified values (7 or 11 elements per sample), and the physical dimensions of the samples, mean that they cannot be used for 61 elements and for as wide a range of analytical schemes as implied by Morrison.

Further, the Canadian Association for Applied Spectroscopy (now the Spectroscopy Society of Canada) transferred the work of its former Committee on Non-metallic Standards to the Mines Branch (now the Canada Centre for Mineral and Energy Technology) a number of years ago. The work is now carried on as the Canadian Certified Reference Materials Project, which has produced some 40 reference materials, but very few of those (three rocks and four soils) have a significant number of firmly established values for trace elements. As for the Geological Institute of Bulgaria, its one and only granite reference sample was first mentioned by Flanagan (1970), but no quantitative data on that sample appeared until reported by Ivanov (1981), with replicate data (not enough to establish firm recommended values) on only some 13 trace elements – hardly a reliable "calibration standard". The Geological Survey of Tanzania (actually the Mineral Resources Division) produced one Tonalite sample, T-1, but its supply was reported as exhausted by Flanagan (1973).

The foregoing inaccuracies in Morrison's report might be dismissed as a mere unfortunate combination of oversights, but at least three other examples can be cited, all of which tend to suggest that many authors of otherwise very good work have not given sufficient attention to their overviews of geological reference materials.

In their excellent book on Trace Element Analysis of Geological Materials, Reeves and Brooks (1978) listed a large number of "Reference Standards", but neglected to mention that, e.g. the Pennsylvania State University's feldspar samples have been established on the basis of analysis in only one laboratory (admittedly a very good one); that as of 1978, there were no published recommended values for USGS rocks BHVO-1, MAG-1, QLO-1, RGM-1, SCo-1, SDC-1, SGR-1 and STM-1; that the four samples from Queen Mary College, London, are apparently no longer available; that all of the NBS samples of clays, feldspars, etc. have very few, if any, certified values for trace elements; that the same is true of the G. Frederick Smith Chemical Company's series of limestone-dolomite blends; that the same is true of most of the British Chemical Standards samples; that the few reference materials from the Universities of Basel and Bern are available only in 5-gram quantities; that several other samples in their list, from various sources, are no longer available; etc., etc.

Sandell and Onishi (1978), although their book is concerned with Photometric Determination of Traces of Metals, listed many reference samples as "Geochemical Standards", some of which have few, if any, reliable trace-element values. To their credit, it must be pointed out that Sandell and Onishi, in their Table 4-4, indicate which of the listed samples were no longer available at their time of writing. Otherwise, their list exhibited many of the shortcomings attributed above to the tabulation by Reeves and Brooks (1978).

In their text-book on rock analysis, Jeffery and Hutchison (1981) published a similar list of "Standard Geochemical Reference Materials". They cannot be faulted for the fact that many items in their list are of little or no value in trace-element analysis for the simple reason that they are concerned with the determination of major and minor elements as well. However, they did not mention that 11 of the 16 USGS samples in their list had no published recommended values; their list also displays other limitations overlooked by Reeves and Brooks (1978) and by Sandell and Onishi (1978).

It was stated earlier (Abbey, 1980) that "...the time, effort and money going into the establishment of reliable values for reference samples is not universally appreciated or even understood". To that, one might now add that among the significant characteristics of reference samples for rock and mineral analysis are not only the sample type and composition (as far as is known), but also the specific constituents for which values are established to a sufficient degree for each intended application, not to mention the quantities (if any) available, their cost, etc. The last items are among the most important; samples have been known to be supplied in quantities varying from less than a gram to as much as 200 grams, at costs ranging from no charge to about $200.

In this work, it was decided to include only such materials as can be useful in connection with the general analysis of silicate rocks. Additional criteria were: (a) that the material be available in sufficient quantity, and (b) that reliable compositional values be available for a reasonable number of constituents. It soon became evident that criterion (a) would probably be ignored in cases where the original supply of a particular sample had been exhausted, but where considerable quantities might still be found on the shelves in many laboratories.

The reference materials listed in the following pages may be divided into three broad categories:

(i) silicate rocks with compositional values for most major and minor constituents, and for a reasonable number of trace elements (including samples of such compositionally similar silicate minerals as feldspars and micas);

(ii) rocks and other materials of rock-like composition with compositional values for a limited number of constituents (most frequently for trace elements); and

(iii) naturally-occurring or man-made materials with compositional values for the normal major and minor constituents of silicate rocks, but differing from them significantly in concentration.

Materials in category (i) are, naturally, the most useful. Category (ii) includes materials such as sands, soils, sediments, fly ash, glasses, etc. In category (iii) are slags, refractories, iron ore, clays, etc. It should be noted that the boundaries between the three categories are not intended to be rigidly drawn, in particular between (ii) and (iii). Materials in those two categories can be very useful in providing high and low points in calibrations and other applications. However, such materials frequently have both physical and chemical characteristics that distinguish them markedly from rocks – i.e. they may be subject to interferences in some methods because of unusually high concentrations of certain elements or because of the presence of organic matter; they may be difficult to fuse or to subject to other chemical attack, etc.

Among the materials not included in this work are rocks and minerals of rock-like composition which have never been available for general distribution, or have been available in very limited quantities; similar materials with reliable values for only a few constituents, designed for special application; ores of precious, base or rare metals for which only "information values" are available for the normal rock constituents, etc. Mention is made of a few such materials in this work, but few details are given. In many cases, the producers of some of the materials included here may also be sources of excluded materials. Interested readers should be able to obtain further information directly from such sources.

In Table 7, all of the materials mentioned in subsequent tables are listed alphabetically, according to sample type, including a few for which reliable values have not been published at time of writing, but may be expected in the foreseeable future. Flanagan (1970) warned that with the unco-ordinated proliferation of reference materials from many different sources, there was an ever-growing danger of duplication of designations. Such duplication finally occurred when the International Atomic Energy Agency issued a lake sediment sample designated SL-1, after the Canadian Certified Reference Material Project had designated their slag sample as SL-1. To avoid confusion in this work, the lake sediment sample is identified as SdL-1, the slag sample as SLg-1.

Table 7. Listing of samples according to type of material

Sample type	Samples
Aleurolite	SA-1
Andesite	AGV-1, JA-1
Anorthosite	AN-G
Ash	IS-1, NBS-1633, -1633a, WIA-1
Basalt	BB-1, BBM-1, BCR-1, BE-N, BHVO-1, BIR-1, BM, BR, JB-1, -2, NBS-688
Bauxite	BCS-395, BX-N, NBS-69b, -696, -697, SB-1, -2
Calc-silicate	M-3
Clay	KK, NBS-97a, -98a, SDO-1 (USSR)
Diabase	DNC-1, W-1, -2
Diorite	DR-N
Dolerite	I-3, S-18
Dunite	DTS-1, -2, NIM-D
Feldspar	AL-I, BCS-375, -376, FK-N, NBS-70a, -99a
Gabbro	GOG-1, GSM-1, MRG-1, SGD-1A
Glass	NBS-91, VS-N
Glauconite	GL-O
Granite	G-1, -2, GA, G-B, GB-1, GH, GM, GR, Gran-1, GS-N, I-1, MA-N, NIM-G, S-16, SG-1A, -2,
Granodiorite	GSP-1, JG-1
Greisen	GnA, MA-N
Iron-rich	ES-681-1, FeR-1 to -4, IF-G
Jasperoid	GXR-1
Kimberlite	S-7
Kyanite	DT-N
Larvikite	ASK-1
Latite	QLO-1
Lujavrite	NIM-L
Marl	MO8-1
Mica	Mica-Fe, -Mg
"Mill-head"	GXR-4
Nepheline ore	SNS-1
Norite	NIM-N
Obsidian	NBS-278
Peridotite	PCC-1
Pyroxenite	NIM-P
Quartz	S-17
Rhyolite	RGM-1
Sand	FK, NBS-81a, -165a, SS
Schist	ASK-2, M-2, S-12, -13, SDC-1
Sediment	BCSS-1, GSD-1 to -8, GXR-3, LKSD-1 to -4, MAG-1, MESS-1, NBS-1645, PSJ-1, S-14, -19, -20, SdL-1, SDO-2, STSD-1 to -4
Serpentine	S-15, SW, UB-N
Shale	KnC-ShP-1, S-9, SCo-1, SDO-1 (USA), SGR-1, TS
Silica	BCS-267, -313, NBS-81a, NBS-165a, S-17, SS
Sillimanite	BCS-309
Slag	BCS-367, ES-878-1, SLg-1
Slate	TB
Soil	GXR-2, -5, -6, S-10, SO-1 to -4, SOIL-5, SP-1 to -3
Syenite	NIM-S, NS-1, SNS-2, STM-1, SY-2, -3
Tonalite	T-1, TLM-1
Trap	ST-1A

A similar duplication subsequently occurred between a U.S. shale SDO-1 and a USSR clay SDO-1. In this case, no information on composition was available to the writer for either sample, so no attempt was made to assign new designations. The samples are listed in some tables for information only.

All of the materials in Table 7 also appear in Table 8, but in alphabetical order of their individual designations. Material types are stated more specificly in Table 8, where the samples are also identified with institutions and countries of origin and referred to pages in the text for more detailed information.

In Tables 9-50, a distinction is made between listed concentration values recommended by the originators of the samples and those derived by this compiler. In the former case, information is given (if known) about the derivation method used. In the latter case, explanations are given on why the compiler's derived values are used.

Most of the terms used in Tables 9-50 have been explained earlier in this report, but they are now presented again to facilitate use of those tables:

(i) All major and minor constituents (except fluorine and sulphur) are reported as the conventional oxides, with concentrations expressed in per cent.

(ii) The constituents mentioned in (i) have been calculated to the dry basis wherever H_2O^- values were reported. Where H_2O^- values were not available, reported values were taken as being on the dry basis.

"Dry basis", unless otherwise specified, refers to the state of a sample, dried to constant weight at 105-110°C. In some cases, special drying conditions at various temperatures are specified by the originators; those conditions are given in the descriptions of the samples concerned.

(iii) All "trace elements" (here defined as all constituents other than those in (i) and (ii)) are expressed as ppm (micrograms per gram), except where otherwise indicated.

(iv) "others" refers to the sum of trace elements, each converted to the appropriate oxide, except for non-carbonate carbon, chlorine, bromine, iodine and nitrogen, which are added in as elements.

(v) "O/F,S,Cl" represents the oxygen subtracted, equivalent to the fluorine, sulphur and chlorine contents, using the factors 0.421 for F, 0.5 for S (Peck, 1964), 0.226 for Cl.

(vi) "Sum (corr.)" is the corrected sum, after applying the preceding step. Its closeness to 100 per cent is a criterion of the validity of the derivation procedure, of the accuracy of the raw data, or of both, but there are reservations regarding this criterion, as mentioned earlier in this report.

(vii) Fe_2O_3TR is the derived value for total iron, expressed as ferric oxide, based on reported results for total iron.

(viii) Fe_2O_3TC is the value for total iron, expressed as ferric oxide, but calculated from the derived values for Fe_2O_3 and FeO, each of which is based on reported results for ferric and ferrous iron respectively.

(ix) Closeness of Fe_2O_3TR and Fe_2O_3TC to one another is also a criterion of the validity of the derivation procedure, of the accuracy of the raw data, or of both.

x) There are two circumstances under which this"ferric-oxide compatibility" test cannot be applied:

(a) where ferrous iron could not be determined or where insufficient data were available to derive separate ferrous and ferric values;

(b) where the originators did not derive a value for ferric iron as such, but calculated their "best value" for ferric iron by difference between the derived values for total iron and ferrous iron. Such ferric values are shown as Fe_2O_3C.

(xi) Where separate values cannot be shown for Fe_2O_3 and FeO, Fe_2O_3T is shown in the tabulation.

(xii) Where separate values cannot be shown for H_2O^+ and CO_2, LOI (loss on ignition) is shown, if known.

(xiii) Use of the question mark has been explained earlier, in connection with the select laboratories method. With values derived by originators using other methods, there is generally a division between more and less reliable values. The question mark, in such cases, has been applied to the less reliable values, although subjective judgment is involved in some cases. It follows that the significance of the question mark may vary in going from one group of reference samples to another. Values listed with question marks should be avoided in applications where only one reference sample is used at one time. On the other hand, they may prove useful when used in combination with "unquestioned" values – e.g. in calibrations.

(xiv) Values shown in Tables 9-50 in parentheses are intended "for information only" – i.e. to give a general idea of overall composition. They should not be used as reference or calibration values under any circumstances. For that reason, they are not listed in the "concentration ladders" in Part III of this report. The same is true with some samples where only "information values" are available for all constituents.

Uncertainty values are available in the original references for the usable values for some, but not all, of the samples in the Tables. It must be remembered that not all assigned uncertainties are necessarily based on the same principle – i.e. whether they represent one or more standard deviations (or any other parameter) of all reported results, or of a select group of results. In order to avoid possibly unfair comparisons between uncertainties based on different approaches, and between samples with and without published uncertainty limits, it was decided to omit all information on uncertainties in Tables 9-50, with the exception of the use of question marks and parentheses, as described above.

Readers requiring more specific information on the uncertainties of listed values are urged to consult the original reference in each case, not only to learn the magnitudes of the various uncertainty limits, but also to ascertain how they were computed.

Table 8. Alphabetical listing of the samples

Sample No.	Description	Source	Ref. page
AGV-1	Andesite	USGS (USA)	29
AL-1	Albite	GIT-IWG (France)	50
AN-G	Anorthosite		49
ASK-1	Larvikite	ASK (Scandinavia)	42
-2	Schist		
BB-1	Basalt	FUB (Brazil)	69
BBM-1	Basalt	USGS (USA)	34
BCR-1	Basalt		29
BCS -267	Silica Brick	BAS (UK)	40
-309	Sillimanite		
-313	Pure Silica		
-367	Blast Furnace Slag		
-375	Soda Feldspar		
-376	Potash Feldspar		
-395	Bauxite		
BCSS-1	Marine Sediment	NRC (Canada)	27
BE-N	Basalt	GIT-IWG (France)	49
BHVO-1	Basalt	USGS (USA)	31
BIR-1	Basalt		32
BM	Basalt	ZGI (East Germany)	55
BR	Basalt	CRPG (France)	45
BX-N	Bauxite	ANRT (France)	45
DNC-1	Diabase	USGS (USA)	32
DR-N	Diorite	ANRT (France)	45
DT-N	Kyanite		
DTS-1	Dunite	USGS (USA)	29
-2	Dunite		34
ES -681-1	Iron ore	BAS (UK)	40
-878-1	Blast Furnace Slag	IRSID (France)	43
FeR-1	Iron-formation Rock	CCRMP (Canada)	25
-2			
-3			
-4			
FK	Feldspar Sand	ZGI (East Germany)	55
FK-N	Potash Feldspar	ANRT (France)	46
G-1	Granite	USGS (USA)	27
-2	Granite		29
GA	Granite	CRPG (France)	45
G-B	Granite	IGB (Bulgaria)	52
GB-1	Granite	FUB (Brazil)	69
GH	Granite	CRPG (France)	45
GL-O	Glauconite	ANRT (France)	46
GM	Granite	ZGI (East Germany)	55
GnA	Greisen		
NBS-69b	Bauxite	NBS (USA)	35
-70a	Potash Feldspar		
-81a	Glass Sand		
-91	Opal Glass		
-97a	Flint Clay		
-98a	Plastic Clay		
-99a	Soda Feldspar		
-165a	Glass Sand		
-278	Obsidian		
-688	Basalt		
-696	Bauxite		
-697			
-1633	Fly Ash		
-1633a	Fly Ash		
-1645	River Sediment		
NIM-D (SARM -6)	Dunite	NIM (South Africa)	64
-G (-1)	Granite		
-L (-3)	Lujavrite		
-N (-4)	Norite		
-P (-5)	Pyroxenite		
-S (-2)	Syenite		
NS-1 (KG-1 etc.)	Nepheline Syenite	LEN (USSR)	56
PCC-1	Peridotite	USGS (USA)	29
PSJ-1	Pond Sediment	NIES (Japan)	63
QLO-1	Quartz Latite	USGS (USA)	31
RGM-1	Rhyolite	USGS (USA)	31
S -7	Kimberlite	NIM (South Africa)	67
-9	Carbonaceous Shale		
-10	Soil		
-12	Sillimanite Schist		
-13	Garnet Schist		
-14	Stream Sediment		
-15	Serpentinite		
-16	Fluor-rich Granite		
-17	Quartz		
-18	Dolerite		
-19	Stream Sediment		
-20	Stream Sediment		
SA-1	Aleurolite	IGI (USSR)	58
SB-1	Bauxite		
-2	Bauxite		
SCo-1	Cody Shale	USGS (USA)	31
SDC-1	Mica Schist		
SdL-1	Lake Sediment	IAEA (International)	51
SDo-1 (USA)	Shale	USGS (USA)	34

Table 8 (cont'd)

Sample No.	Description	Source	Ref. page
GOG-1	Ophiolite Gabbro	Gruppo Ofioliti (Italy)	68
GR	Granite	CPPG (France)	45
Gran-1	Granite	WACOM (Netherlands)	69
GSD-1	Stream Sediments	IGGE (China)	59
-2			
-3			
-4			
-5			
-6			
-7			
-8			
GSM-1	Gabbro	USGS (USA)	34
GS-N	Granite	ANRT (France)	46
GSP-1	Granodiorite	USGS (USA)	29
GXR-1	Jasperoid	USGS-AEG (USA)	35
-2	Soil		
-3	Hot Spring Deposit		
-4	Copper Mill-head		
-5	Soil		
-6	Soil		
I-1	Aplitic Granite	QMC (UK)	41
I-3	Dolerite		
IF-G	Iron-formation Rock	GIT-IWG (France)	50
IS-1	Incinerated Sludge	CCIW (Canada)	26
JA-1	Andesite	GSJ (Japan)	60
JB-1	Basalt		
-2	Basalt		
JG-1	Granodiorite		
KK	Kaolinite	UNS (Czechoslovakia)	52
KnC-ShP-1	Purington Shale	Knox College (USA)	69
LKSD-1	Lake Sediments	CCRMP (Canada)	26
-2			
-3			
-4			
M-2	Pelitic Schist	QMC (UK)	41
M-3	Calc-silicate		
MAG-1	Marine Sediment	USGS (USA)	31
MA-N	Granite	GIT-IWG (France)	49
MESS-1	Marine Sediment	NRC (Canada)	27
Mica-Fe	Biotite	CRPG (France)	45
Mica-Mg	Phlogopite		
MO8-1	Ferriferous Marl	IRSID (France)	43
MRG-1	Gabbro	CCRMP (Canada)	24
SDo-1 (USSR)	Terrigene Clay	IGI (USSR)	58
-2	Terrigene Mud		58
SG-1A (2005)	Albitized Granite		57
-2	Alaskite Granite		58
SGD-1A (2003)	Gabbro		57
SGR-1	Petroleum Shale	USGS (USA)	31
SLg-1	Blast Furnace Slag	CCRMP (Canada)	25
SNS-1	Nepheline Ore	IGI (USSR)	52
-2	Nepheline Syenite		
SO-1	Soil	CCRMP (Canada)	25
-2			
-3			
-4			
SOIL-5	Soil	IAEA (International)	51
SP-1	Black Earth	? (USSR)	58
-2	Soil		
-3	Soil		
SS	Glass Sand	UNS (Czechoslovakia)	52
ST-1A (2001)	Trap	IGI (USSR)	57
STM-1	Syenite	USGS (USA)	31
STSD-1	Stream Sediment	CCRMP (Canada)	26
-2			
-3			
-4			
SW	Serpentinite	ZGI (East Germany)	55
SY-2	Syenite	CCRMP (Canada)	24
-3			
T-1	Tonalite	MRT (Tanzania)	63
TB	Slate	ZGI (East Germany)	55
TLM-1	Tonalite	USGS (USA)	34
TS	Shale	ZGI (East Germany)	55
UB-N	Serpentine	ANRT (France)	45
VS-N	Synthetic Glass	ANRT (France)	46
W-1	Diabase	USGS (USA)	27
-2	Diabase		32
WIA-1	Waste Incinerator Ash	BAM (West Germany)	69

CCRMP – CANADIAN CERTIFIED REFERENCE MATERIALS PROJECT

(Contact: Dr. H.F. Steger, Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada, 555 Booth St., Ottawa, Canada K1A OG1)

The work of this group originated as a Non-Metallic Standards Committee of the then Canadian Association for Applied Spectroscopy. Subsequently, the name of the latter was changed to the Spectroscopy Society of Canada; later, the work on reference materials was transferred to the then Mines Branch (now the Canada Centre for Mineral and Energy Technology, or CANMET), where it was re-organized as the Canadian Certified Reference Materials Project. The CCRMP is now administered by CANMET staff, but the co-ordinating committee includes representatives from the Geological Survey of Canada, other governmental departments, and private industry.

Most of the reference samples available from CCRMP are ores and related metallurgical materials. Details may be found in a catalog by Steger (1980). A few metal and alloy samples are also available.

CCRMP rocks

Two supposed "standard rocks", SY-1 and SU-1, were prepared a number of years ago. SY-1 was a syenite from the Bancroft area of eastern Ontario, containing unusually high concentrations of radioactive minerals. SU-1 was actually a sulphide ore from the region of Falconbridge, Ontario, but was regarded as a mineralized rock. Although neither sample was ever subjected to a systematic collaborative analysis from which reliable values could be deduced, three compilations of data were published (Anonymous, 1961; Webber, 1965; Sine et al., 1969). The laboratories of the Analytical Chemistry Section, Geological Survey of Canada, contributed a limited quantity of analytical data.

Supplies of SU-1 and SY-1 were limited, and both were soon exhausted. SU-1 was eventually succeeded by SU-1a, but only as a nickel-copper-cobalt ore, with additional recommended values for silver, platinum and palladium.

SY-2 is another syenite, collected from what was thought to be the same source as that of SY-1. However, preliminary analysis showed that SY-2 contained far less of uranium, of thorium and of the rare earths than did SY-1. A third collection from the same location was then blended, by means of autogenous grinding, with a radioactive concentrate, rich in allanite, betafite and uraninite, and the resulting product designated SY-3. Subsequent analytical data suggested that the autogenous grinding had resulted in a small degree of heterogeneity, but further analysis failed to confirm or refute the suggestion.

MRG-1 is a gabbro, collected on the slopes of Mount Royal, in Montreal. Geological background of the sample was described in detail by Perrault et al. (1974).

Systematic collaborative analysis co-ordinated by the GSC Analytical Section, resulted in a "comprehensive" report (Abbey, 1979); the recommended values are reproduced in Table 9. All of them were derived by the select laboratories method. As mentioned earlier, a rough estimate was made of the relative reliability of each usable value, details being given in Abbey (1979).

UM-1, UM-2 and UM-4 are described (Steger, 1980) as "sulphide-bearing ultramafic rocks". They have provisional values for copper, nickel and cobalt, on the basis of a leach test using ascorbic acid and hydrogen peroxide. Evaluation for those tests was the responsibility of the GSC Geochemistry Section. These samples are not intended for use as rock reference materials.

Table 9. CCRMP rocks – usable values (compiler's)

Per cent (dry basis)	Syenite SY-2	Syenite SY-3	Gabbro MRG-1
SiO_2	60.10	59.68	39.32
TiO_2	0.14	0.15	3.69
Al_2O_3	12.12	11.80	8.50
Fe_2O_3	2.28	2.44	8.26
FeO	3.62	3.58	8.63
MnO	0.32	0.32	0.17
MgO	2.70	2.67	13.49
CaO	7.98	8.26	14.77
Na_2O	4.34	4.15	0.71
K_2O	4.48	4.20	0.18
H_2O^+	0.43	0.42	0.98
CO_2	0.46	0.38	1.00
P_2O_5	0.43	0.54	0.06
F	0.51	0.66	0.025
S	0.011	0.005	0.06
Others	0.43?	1.18?	0.33?
Sum	100.35?	100.48?	100.18?
O/F, S, Cl	0.22?	0.31?	0.04?
Sum (corr.)	100.13?	100.17?	100.14?
Fe_2O_3TR	6.28	6.42	17.82
Fe_2O_3TC	6.30	6.42	17.85
ppm			
Ag			0.14?
As	18	20	0.7
B	85?	110	13?
Ba	460	430	50?
Be	23	22	0.6?
C (non-$CO_3^=$)	270?	250?	250?
Ce	210?	2200	25?
Cl	130?	140?	150?
Co	11	12	86
Cr	12	10	450
Cs	2.3?	2.5?	0.6?
Cu	5	16	135
Dy	20?	80?	3?
Er	12?	50?	
Eu	2.4?	14?	1.4?
Ga	28	26	18?
Gd		55?	
Hf	8?	9?	
Ho		20?	0.5?
La	88	1350	10?
Li	93	92	4
Lu	3?	8?	0.2?
Mo	3?	2.5?	
Nb	23?	130	20?
Nd	71?	800?	19?
Ni	10	11	195
Pb	80	130	10
Pr		120?	
Rb	220	208	8
Sb	0.2	0.3	0.4
Sc	7?	7?	48?
Sm	15?	100?	5?
Sn	4	6?	3.2
Sr	275	306	260
Tb	2?	11	
Th	380?	990	1?
Tm	2?	8?	0.1?
U	290	650	0.3?
V	52	51	520
Y	130	740	16?
Yb	17	65	1?
Zn	250	240	190
Zr	280	320	105

A number of bulk samples of iron formation rocks were collected in the 1981 field season (McLeod et al., 1982). After preliminary analyses, four were selected for processing as reference materials. Of those, FeR-1 is from Austin Brook, near Bathurst, New Brunswick; FeR-2 is from the Griffith Mine, Bruce Lake, Ontario; FeR-3 and FeR-4 are from the Sherman Mine, Temagami, Ontario. Collection of the samples was the responsibility of the Mineral Deposits Section, Economic Geology Division, GSC; crushing, grinding, homogenization, bottling and sample distribution were performed by the Mineral Science Laboratories, CANMET; the inter-laboratory collaborative evaluation was co-ordinated by the Analytical Chemistry Section, GSC.

At this writing, collaborative analysis of the FeR samples is still underway and will not likely reach a point where usable values can be deduced for some time to come.

CCRMP soils

Four samples of soils, collected by the Land Resource Research Institute, Agriculture Canada, were prepared at CANMET for use as reference samples. Of those, SO-1 is described as a Regosolic clay soil, collected near Hull, Quebec; SO-2 is a Podzolic B horizon soil, from the Montmorency Forest, north of Quebec City; SO-3 is a calcareous C horizon soil, collected near Guelph, Ontario; SO-4 is a Chernozemic A horizon soil, from northeast of Saskatoon, Saskatchewan. The analytical evaluation was carried out in accordance with the scheme of Sutarno and Faye (1975). GSC Analytical Section laboratories were not involved. Details may be found in the report by Bowman et al. (1979). The values shown in Table 10 are based on that report, but have been re-cast in the form usually used in rock analysis.

Values shown with question marks in Table 10 are those described by Bowman et al. as "for information only". The originators gave 95 per cent confidence limits with all of their recommended values, but they admitted that "...some subjectivity was required in identifying outliers..." and that "...it is evident that the capability of the analyst is the most important factor in determining the reliability of results as both good and poor data were generated by all methods...". Unfortunately, their classification of "methods" is far from specific – generally merely involving the technique of final measurement. Still, the emphasis on who did an analysis, rather than how it was done may be regarded as one of the foundations of the select laboratories method; one might then conclude that the rigorous Sutarno and Faye (1975) scheme, which works so well with ores, is not really suitable with multi-component materials of highly variable composition, such as soils.

The persistently low summations in Table 10 might lend some credence to the foregoing conclusion. An attempt was therefore made to calculate usable values by means of the select laboratories method, but there was no resulting improvement in the summations. A more logical conclusion might therefore be: Soils Are Different! Just as an evaluation scheme which works well for ores will not necessarily be effective for rocks, perhaps the scheme that works so well for rocks may not be suitable for soils.

In a sense, a soil might be regarded as a rock-like material containing particularly high concentrations of organic matter, but certain significant rock constituents are missing from the analyses of these soils – i.e. H_2O^+, carbonate carbon, ferrous and ferric iron, etc. Further, the purpose of the analysis of soils may also result in some differences in the results – i.e. the constituents of interest for agricultural studies will not necessarily coincide with those of interest in the geological sciences.

Table 10. CCRMP soils – usable values (originators')

Per cent (dry basis)	SO-1	SO-2	SO-3	SO-4
SiO_2	55.02	53.46	33.93	68.5?
TiO_2	0.88	1.43	0.32?	0.57
Al_2O_3	17.72	15.24	5.76	10.32
Fe_2O_3T	8.58	7.95	2.16	3.39
MnO	0.11	0.09	0.07	0.08
MgO	3.83	0.90	8.47?	0.93
CaO	2.52	2.74	20.47?	1.55
Na_2O	2.56?	2.35?	1.00	1.31?
K_2O	3.23	2.95	1.40	2.08
LOI	4.4?	11.5?	25.3?	10.4?
P_2O_5	0.14	0.69?	0.11?	0.21
F	0.07?	0.05?	0.03?	0.03?
S	0.01?	0.03?	0.02?	0.04?
Others	0.27?	0.31?	0.10?	0.19?
Sum	99.33?	99.69?	99.37?	99.60?
O/F, S, Cl	0.04?	0.04?	0.02?	0.03?
Sum (corr.)	99.29?	99.65?	99.35?	99.57?
ppm				
As	1.9?	1.2?	2.6?	7.1?
B			22?	
Ba	900?	1000?	280?	780?
C (total, pct)	0.25?	4.8?	6.6?	4.4?
Cd	0.15?	0.18?	0.14?	0.42?
Co	33?	13?	12?	15?
Cr	160	16	26	61
Cu	61	7	17	22
Hg	0.022	0.082	0.017	0.03?
La	56?			
Li	40?	9?		
Mo		2?		
N (total, pct)	0.04?	0.22?		0.4?
Ni	94	12?	16	26
Pb	21	21	14	16
Rb	145?	81?	41?	75?
Sc	19?			
Sr	300?	340	220	170
V	140	64	44?	90
Y	24?	40?	17?	23?
Zn	145	125	52	94
Zr	81?	790?	150?	310?

Nevertheless, with suitable precautions to allow for the high organic contents, these soil samples may prove useful in rock analysis because of their usable values for certain trace elements.

CCRMP slag

Other CCRMP materials may be of use in rock analysis (see Steger, 1980), but only the blast furnace slag is included here because its high calcium, low silica and high manganese contents may prove useful in calibrations. The sample is designated by the originators as SL-1, but is referred to as SLg-1 in this work, to avoid confusion with the International Atomic Energy Agency's lake sediment, also SL-1, but listed herein as SdL-1.

Table 11. CCRMP slag – usable values (originators')

Per cent	SLg-1
SiO_2	35.73
TiO_2	0.38?
Al_2O_3	9.63
*FeOT	0.92
MnO	0.86?
MgO	12.27
CaO	37.48
Na_2O	0.39?
K_2O	0.51?
†P_2O_5	(0.02)
S	1.26
Others	0.01?
Sum	99.46?
ppm	
†Cr	(60)
†V	(20)

* Total iron, expressed as FeO
† Not usable values

The values in Table 11 are those of Mason and Bowman (1977), the ones with question marks being their "provisional values", presumably the constituents which failed to meet the "certification factor" requirements (Sutarno and Faye, 1975). The values in parenthesis are "for information only".

Individual results listed by Mason and Bowman (1977) are much more coherent than those for the soil samples (Bowman et al., 1979), suggesting analytical conditions similar to those with ores, more than those with soils or rocks. Although the analytical conditions resulted in values with relatively narrow confidence limits, it should be noted that the summation is somewhat low. If the oxygen-for-sulphur correction were applied (assuming all sulphur to be present as sulphide), the summation would fall under 99 per cent, suggesting that not all constituents had been accounted for. Among other possible constituents, appreciable non-carbonate carbon is reportedly present (J. Kelly, Steel Company of Canada, personal communication). The GSC Analytical Section was not involved in the evaluation.

Other CCRMP materials

Eight proposed reference samples of geochemical interest are in preparation, at time of writing, for eventual distribution as CCRMP materials. The Geochemistry Subdivision of the Geological Survey of Canada is co-ordinating the collection, processing and evaluation of those samples, some of the original materials having been contributed by the British Columbia Ministry of Energy, Mines and Petroleum Resources. The suite will consist of four lake sediments, LKSD-1 to -4, and four stream sediments, STSD-1 to -4. Plans are also being made to prepare a suite of four soil samples. All of the foregoing samples are to be evaluated mainly for concentrations of trace elements of general geochemical interest.

Some CCRMP ore samples (Steger, 1980) may prove useful in certain aspects of rock analysis, but it must be remembered that all of them have been rigorously evaluated for only a limited number of constituents, other compositional values for them being "for information only".

Table 11A. CCIW incinerated sludge IS-1 – usable values (originators')

	Per cent
SiO_2	32.1
TiO_2	1.02
Al_2O_3	7.18
Fe_2O_3T	18.6
MnO	0.19
MgO	3.8
CaO	12.5
Na_2O	0.78
K_2O	1.4
P_2O_5	11.5
SO_3	1.8
Others	3.5?
Sum	94.4?

	Per cent	ppm
As		40
Ba	0.19	
Cd		9
Cr	0.52	
Cu	0.25	
Mo		57
Ni		640
Pb	0.16	
Sn	0.19	
V		77?
Zn	1.4	

CCIW – CANADA CENTRE FOR INLAND WATERS

(Contact: K. Aspila, Wastewater Technology Centre, Burlington, Ont., Canada L7R 4A6)

This group has prepared several reference materials for use in their studies in wastewater treatment. Of those, their incinerated sludge (referred to herein as IS-1) could prove useful in connection with rock analysis. Knechtel and Fraser (1980) described the preparation and evaluation of the sample. For every constituent reported by participating analysts, Knechtel and Fraser listed the number of reporting analysts, the average value and standard deviation, after the elimination of outliers by the Grubbs (1969) test. They also provided recommended values and uncertainties (probably standard deviations) based only on those determinations resulting in measurements on the whole sample – i.e. excluding data on solutions from incomplete decompositions.

The values for IS-1 have been converted to a rock-like format, and are shown in Table 11A. The questioned value for vanadium is the "average" of Knechtel and Fraser, which they did not list as a recommended value, possibly because of the large standard deviation. Their "average" table also included four additional elements (beryllium, mercury, selenium and zirconium), for each of which fewer than five results were available, and no values were therefore recommended.

The low summation suggests that other constituents may be present, possibly volatile matter that might be revealed by a loss on ignition.

GSC Analytical Chemistry laboratories contributed some data in the evaluation of this sample.

NRC – NATIONAL RESEARCH COUNCIL OF CANADA

(Contact: Dr. S.S. Berman, Chemistry Division, National Research Council, Montreal Road, Ottawa, Canada K1A 0R9)

Two marine sediment materials were obtained from the Gulf of St. Lawrence, BCSS-1 from the Baie des Chaleurs, and MESS-1 from the estuary of the Miramichi River. The samples were evaluated essentially by the "in-house" method, with only small contributions from other laboratories and none from the GSC. Confidence limits at the 95 per cent level were established by a combination of statistical and subjective considerations. The values listed in Table 12 are those of Berman (1981).

Values shown with question marks in Table 12 were described by Berman (personal communication) as "less reliable... for information only". Those in parentheses are the results of semi-quantitative analysis by spark-source mass spectrometry. While the former values may prove useful when used in combination with better-established values in other reference materials, the latter should not be considered usable under any circumstances. Many of the values in Table 12 have been subjected to a rounding procedure, in order to facilitate comparison with other reference materials in this report.

The low summations may be due to the presence of volatile matter not accounted for as carbon, sulphur, etc. The large uncertainties in many of the trace elements are not likely to account for the deficiencies in the summations. It should be remembered, however, that these materials were prepared for use in environmental studies, with geochemical applications as possible secondary interests. They should therefore not be judged in terms of requirements for reference materials for general rock and mineral analysis, but they will likely be useful in the determination of some trace elements. There is good reason to believe that the listed values are of high quality, particularly if one takes into account the uncertainty limits given in the original publication (Berman, 1981).

USGS – UNITED STATES GEOLOGICAL SURVEY

(Contact: F.J. Flanagan, Liaison Officer, Geological Survey, U.S. Deparment of the Interior, Reston, Va. 22092, U.S.A.)

As mentioned earlier in this paper, the U.S. Geological Survey must be regarded as the real pioneers in the subject of reference materials for rock and mineral analysis, particularly in connection with the work on G-1 and W-1. No fewer than 19 different reference samples from USGS are described in some detail in the following pages. Others are known to exist, of which a few are mentioned at the end of this section of this report; information on some additional ones is not available at this writing. The 19 samples about to be described may be conveniently considered as a series of "generations" – USGS I, USGS II, etc.

USGS I

The importance of samples G-1 and W-1 has been mentioned earlier in this report in connection with the historical development of the subject of reference materials for the analysis of rocks and minerals. Supplies of G-1 became exhausted before work began on this series of papers (Abbey, 1972, 1973b, 1975b, 1977b, 1980); G-1 was therefore not listed in them. W-1 was available much later (although now exhausted), so its composition was listed in all of the earlier papers. As it is likely that many laboratories still have small quantities of both samples, it was decided to include them in this report, as a matter of record.

Table 12. NRC marine sediments – usable values (originators')

Per cent (dry basis)	Marine Sediments	
	BCSS-1	MESS-1
SiO_2	66.1	67.5
TiO_2	0.734	0.905
Al_2O_3	11.83	11.03
Fe_2O_3T	4.70	4.36
MnO	0.030	0.066
MgO	2.44	1.44
CaO	0.760	0.674
Na_2O	2.72	2.50
K_2O	2.17	2.24
P_2O_5	0.154	0.146
S	0.36	0.72
Others	3.52?	4.02?
Sum	96.92?	94.20?
0/S, Cl, Br, I	0.44?	0.55?
Sum (corr.)	96.48?	93.65?
ppm		
As	11	11
Ba	(330)*	(270)
Be	1.3	1.9
Bi	(0.1)	(0.5)
Br	(210)	(200)
C (total, pct)	2.19	2.99
Cd	0.25	0.59
Ce	(70)	(60)
Cl (pct)	1.12	0.82
Co	11	11
Cr	125	71
Cs	4?	4?
Cu	18.5	25
Dy	(14)	(8)
Er	(8)	(4)
Eu	(2)	(1)
Ga	(23)	(20)
Gd	(11)	(8)
Ge	1.5?	1.7?
Hf	(10)	(20)
Hg	0.13	0.17
Ho	(3)	(2)
I	(100)	(40)
La	(33)	(30)
Li	(20)	(60)
Mo	1.9?	2.2?
Nb	(14)	(20)
Ni	55	30
Pb	23	34
Pr	(7)	(10)
Rb	(80)	(100)
Sb	0.59	0.73
Se	0.4?	0.4?
Sm	(9)	(8)
Sn	(3)	(6)
Sr	96?	89?
Ta	(1)	(2)
Tb	(2)	(1)
Te	(0.3)	(1)
Th	(9)	(20)
Tl	0.6?	0.7?
Tm	(1)	(0.6)
U	(3)	(5)
V	93	72
W	(0.9)	(3)
Y	(50)	(35)
Yb	(7)	(6)
Zn	120	190
Zr	(350)	(500)

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* Values in parentheses are magnitudes only, not usable values.

Table 13. USGS I – usable values (originators')

Per cent (dry basis)	Granite G-1	Diabase W-1
SiO_2	72.68	52.72
TiO_2	0.26	1.07
Al_2O_3	14.05	15.02
Fe_2O_3	0.87	1.40
FeO	0.96	8.73
MnO	0.03	0.17
MgO	0.38	6.63
CaO	1.39	10.98
Na_2O	3.32	2.15
K_2O	5.48	0.64
H_2O^+	0.34	0.53
CO_2	0.07	0.06
P_2O_5	0.09	0.14
F	0.069	0.025
S	*(0.006)	(0.012)
Others	0.29?	0.19?
Sum	100.28?	100.46?
O/F, S, Cl	0.03?	0.02?
Sum (corr)	100.25?	100.44?
Fe_2O_3TR	1.94	11.11
Fe_2O_3TC	1.94	11.10
ppm		
Ag	(0.05)	0.081
As	(0.5)	1.9
Au (ppb)	4?	3.7?
B	(1.7)	(15)
Ba	(1200)	160
Be	(3)	(0.8)
Bi	0.065?	0.046?
Br	(0.4)	(0.4)
Cd	(0.03)	0.15
Ce	(170)	(23)
Cl	(70)	(200)
Co	(2.4)	47?
Cr	(20)	115?
Cs	1.5	0.9
Cu	13	110
Dy	2.4	4
Er	1.15?	2.4
Eu	1.3	1.1
Ga	19.5	16
Gd	(5)	(4)
Ge	1.1	(1.4)

* Values in parentheses are magnitudes only, not usable values

Table 13 (cont.)

ppm	G-1	W-1
Hf	5.2?	2.7?
Hg (ppb)	97?	(220)
Ho	0.35?	0.69?
In	(0.02)	0.065
Ir (ppb)	(0.008)	0.28?
La	100?	9.8?
Li	22?	14.5?
Lu	0.19?	0.35?
Mo	6.5?	0.57?
N	59?	52?
Nb	24	9.5
Nd	56	15
Ni	(1)	76?
Os (ppb)	(0.07)	(0.25)
Pb	48?	7.8?
Pd (ppb)	(2)	(25)
Pr	(19)	(3.4)
Pt (ppb)	(19)	(12)
Rb	220	21
Sb	0.31?	1.0
Sc	2.9?	35?
Se	(0.007)	(0.13)
Sm	8.3?	3.6?
Sn	3.5	3.2
Sr	250	190
Ta	1.5	0.50
Tb	0.54	0.65
Th	50	2.4
Tl	1.25?	0.11
Tm	0.15	0.30
U	3.4?	0.58?
V	17?	260?
W	(0.4)	(0.5)
Y	13	25
Yb	1.05?	2.1
Zn	45	86
Zr	210	105

G-1 has been described (Fairbairn and others, 1951) as coming from the Smith Granite Co., Westerly, Rhode Island. W-1 was from the Bull Run Quarry, near Centerville, Fairfax County, Virginia. The values listed in Table 13 are those of Flanagan (1976c), converted to the dry basis by means of the "best" H_2O^- values in that paper. A few of the trace-element figures have been rounded. The then Mineralogy Division, GSC, contributed major and minor element data for G-1 and W-1.

The values in Table 13 appear to be of good quality in terms of the iron-oxide compatibility test, but the summation of W-1 is rather high. The method used to arrive at these values was not specified by Flanagan (1976c). In verbal communication regarding USGS reference rocks in general, Flanagan has suggested that he uses mean values after rejection of outliers, but the criteria for such rejection appeared to be subjective. Stevens and Niles (1960) had suggested that the "best value" be the mean of the remaining reported values after rejecting all results that differed from the overall mean by more than one standard deviation. However, at least four additional compilations of data on G-1 and W-1 (Fleischer and Stevens, 1962; Fleischer, 1965, 1969; Flanagan, 1976c) have appeared since the work of Stevens and Niles, so it is not clear which approach was used to produce the "best values" of Flanagan (1976c).

In his published lists of "best values", Flanagan (e.g., 1973, 1976b) has categorized values as "recommended", "average" or "magnitude". In Table 13, his "average" values are shown with question marks, his "magnitudes" in parentheses. In view of Flanagan's (1976b) outline of the shortcomings of the G-1/W-1 program, the values in Table 13 should be used with caution – not only those with question marks, but also some which Flanagan listed as "recommended".

USGS II

The six samples in this "generation" are perhaps the most widely used, judging from how often they are quoted in the literature. With the experience in the preparation and evaluation of G-1 and W-1 as a guide, the originators of USGS II were able to avoid a number of pitfalls that raised doubts about the earlier samples. Details were given by Flanagan (1967).

G-2, intended as a replacement for G-1, was collected from the Sullivan quarry, at Bradford, Rhode Island, and like G-1, described as Westerley Granite.

GSP-1, a granodiorite, came from the Silver Plume Quarry, near Silver Plume, Colorado.

AGV-1 is an andesite from Guano Valley, Lake County, Oregon.

BCR-1, a Columbia River basalt, was collected from the Bridal Flow Quarry, Washington.

PCC-1 is a peridotite from East Austin Creek, Sonoma County, California.

DTS-1, a dunite, comes from Hamilton, Washington.

Flanagan (1967), in addition to providing more detailed geological background, described the methods used in preparing the samples and reported analytical data from USGS laboratories for major and minor constituents by both conventional and "rapid" wet chemical methods. Trace element data, based on emission spectrographic analysis in three different USGS laboratories, were also listed.

Although the results from different laboratories and by different methods were generally reasonably close to one another, a few exceptions are worth noting.

In DTS-1, CaO results reported by two different analysts using conventional methods were 0.03 and 0.00 per cent respectively. Three results reported by a four-member "rapid analysis" team (whose CaO results were based on EDTA titration) were 0.10, 0.06 and 0.07 per cent. Assuming that conventional analysis would be more reliable, one might conclude that the lower values of 0.03 and 0.00 were closer to the truth.

The first suspicion that something was wrong arose when CaO was determined by atomic absorption in the course of general analysis of the six samples in our own laboratories, using two different approaches. In one case, the solution used was the product of the earlier stages of a classical analysis – i.e. the sample was decomposed by sodium carbonate fusion; silica and the R_2O_3 group were removed in the usual manner. CaO was determined in the presence of the large excess of magnesium and of the other reagents accumulated in the classical scheme. In the other case, the sample was decomposed by treatment with hydrofluoric and perchloric acids and no separations were made. Both methods gave results that were significantly higher than those by the "rapid methods"!

The first reaction to this unexpected development was to search for possible errors in our atomic absorption procedures, but none could be found. Years later, when sufficient data were available from many other sources, values of 0.14 or 0.15 per cent CaO were recommended for DTS-1 (Abbey, 1978; Flanagan, 1976c), suggesting that the largest error was in the classical analyses! A similar but less pronounced effect was also observed for CaO in PCC-1.

One cannot help but wonder how such an error could occur, particularly since the Denver laboratories of the U.S. Geological Survey (who had reported the low CaO results) are widely recognized as among the world's best for classical rock analysis. A plausible, but by no means certain explanation might lie in assuming that, in view of the very low calcium concentration, an attempt had been made to separate calcium from the re-dissolved magnesium pyrophosphate residue by precipitation as the sulphate in an alcoholic medium. In view of the high Mg/Ca ratio (possibly 500:1), it is conceivable that calcium recovery was incomplete. To this writer's knowledge, nothing has been published by the U.S. Geological Survey about attempts to resolve the contradictions.

A possible object lesson from the foregoing might be that even the best and most reliable analytical methods have limitations, and that the knowledgeable analyst must exercise vigilance in using them.

The other discrepancy in the analysis of USGS II concerned the spectrographic data for trace elements. For all of the samples with concentrations of those elements at detectable levels (i.e. all but PCC-1 and DTS-1), the Menlo Park laboratory reported rubidium results that were much higher than those reported by the other two, and for some of those samples, the Denver results for lithium were noticeably lower than those from the other laboratories. In terms of the "best values" eventually published for lithium and rubidium (Abbey, 1978; Flanagan, 1976c), spectrographic results from both Washington and Denver appeared to be significantly superior to those from Menlo Park.

A more comprehensive compilation of data on USGS II, featuring results from many laboratories, appeared two years later (Flanagan, 1969). As mentioned earlier, that compilation provided the raw material for the development and first application of the select laboratories method (Abbey, 1970). A list of "best values" (Flanagan, 1973) appeared later, and led to the critical comment and reply (Abbey, 1975a; Flanagan, 1975). Still later, Flanagan (1976c) published essentially the same values, but also included a compilation of results reported since the 1969 compilation. Since the 1976 compilation contained no results dated later than 1972, one could conclude that the 1973 and 1976 "best values" were based on all reported results listed in the two compilations (Flanagan, 1969, 1976).

At first, all values for USGS II listed in GSC publications (Abbey, 1970, 1972) were based on the 1969 compilation and the select laboratories method. When the first set of USGS "best values" appeared (Flanagan, 1973), it was decided to use those values in subsequent papers (Abbey, 1973, 1975b, 1977b), on the assumption that the originators might be expected to know more about their samples than did anyone else. However, changes were made where Flanagan's values gave rise to contradictions (Abbey, 1975a). When Flanagan's (1976c) second compilation appeared, the editor of Geostandards Newsletter suggested that the select laboratories method be applied to the combined data from the two compilations. The results of that operation were reported in the same journal (Abbey, 1978) and included in the next general paper in the series (Abbey, 1980).

Values derived by Abbey (1972, 1978) were compared to those of Flanagan (1973, 1976c) in Tables 3 and 4 of this paper, where it appeared that the Flanagan values gave rise to less satisfactory summations and iron-oxide compatibility. In general, his summations tended to run noticeably higher (as it did for W-1 in Table 13), when presented in the form used in the tables in this report. Summations listed in Flanagan's (1973, 1976c) papers had appeared to be lower, possibly because thay had not included all trace-element values.

Usable values for USGS II, based on Abbey (1978), with a few minor corrections, are presented in Table 14. Also included in that table are a few values from Flanagan (1976c), in cases where no usable values were derivable by the select laboratories method. Flanagan's recommended, average and magnitude values are indicated in the same manner as in Table 13.

Table 14. USGS II – usable values (compiler's, except where indicated †)

Per cent (dry basis)	Andesite AGV-1	Basalt BCR-1	Dunite DTS-1	Granite G-2	Granodiorite GSP-1	Peridotite PCC-1
SiO_2	59.61	54.53	40.61	69.22	67.32	42.10
TiO_2	1.06	2.26	0.00?	0.48	0.66	0.01
Al_2O_3	17.19	13.72	0.25	15.40	15.28	0.73
Fe_2O_3	4.56	3.48	1.02?	1.07	1.70	2.54?
FeO	2.03	8.96	6.94?	1.44	2.32	5.17?
MnO	0.10	0.18	0.12	0.03	0.04	0.12
MgO	1.52	3.48	49.80	0.75	0.97	43.50
CaO	4.94	6.97	0.14	1.96	2.03	0.55
Na_2O	4.32	3.30	0.01?	4.06	2.81	0.01
K_2O	2.92	1.70	0.00	4.46	5.51	0.00
H_2O^+	0.78	0.67	0.42	0.50	0.58	4.70
CO_2	0.02	0.02	0.07	0.08?	0.12	0.18
P_2O_5	0.51	0.36	0.00?	0.13	0.28	0.01
F	0.04	0.05	0.00?	0.12	0.37	0.00?
S	0.01?	0.04?	0.00?	0.01?	0.03?	0.01?
Others	0.32?	0.26?	0.93?	0.41?	0.45?	0.75?
Sum	99.93?	99.98?	100.31?	100.12?	100.47?	100.39?
O/F, S, Cl	0.03?	0.04?	0.00?	0.06?	0.18?	0.01?
Sum (corr.)	99.90?	99.94?	100.31?	100.06?	100.29?	100.38?
Fe_2O_3TR	6.78	13.41	8.70	2.69	4.30	8.28
Fe_2O_3TC	6.82	13.44	8.73?	2.67	4.28	8.29?
ppm						
Ag	0.094?	0.034?	0.01?	0.04?	0.083?	0.01?
As	†*(0.8)	0.8?	† (0.03)	† (0.25)	† (0.09)	† (0.05)
Au (ppb)	0.6?	0.8	0.8?	1?	1?	0.7?
B	6?	4		† (2)		† (6)
Ba	1200	680	5?	1900	1300	4?
Be	2?	1.6?		2.4	1?	
Bi	0.05?	0.047?	† 0.01	† 0.043	† 0.037	† 0.013
Br	† (0.5)	0.2?	† (0.2)	† (0.3)		† (0.6)
Cd	† (0.09)	0.09?	† (0.12)	† 0.039?	† (0.06)	† (0.1)
Ce	71	53	† (0.06)	160	360	† (0.09)
Cl	185	58?	11?	100	340	80?
Co	16	36	135	5	7.8	110
Cr	10	15	4200	8	12	2800
Cs	1.3?	0.96	† 0.006	1.4	1	0.025?
Cu	59	16	5	10	33	8
Dy	3.5?	7?	† 0.003	2.3	5.7?	
Er	† (1.2)	3.5?		† (1.3)	† (3)	
Eu	1.6?	2.0	† 0.001?	1.4	2.4?	† 0.002
Ga	21	22	1?	23	23	0.7
Gd	† (5.5)	† 1.55?		5?	†(15)	
Ge	1.2?	1.5	0.9?	1?	0.9?	0.9?
Hf	5?	5	† (0.01)	8?	14?	0.06?
Hg	0.015?	0.007?	0.008?	0.044?	0.016?	0.004?
Ho	† (0.6)	1.2?	† (0.003)	† (0.4)		
In	† (0.04)	0.095?	† (0.0025)	0.032?	† (0.05)	
Ir (ppb)		†(4)	† (1)	0.07?	† (0.012)	6?
La	36	27	† (0.04)	92	195	† (0.15)
Li	12	14	2?	35	30	3?
Lu	0.3?	0.5?	† (0.002)	0.1	0.2?	† 0.006?
Mo	3?	1.5?	1?	0.9?	1.5?	0.5?
N	† 43?	†30?	† 27?	† 56?	† 48?	† 43?
Nb	16?	19?		13?	23?	1?
Nd	37?	26?		58?	190?	
Ni	15	10	2300	3.5	9	2400
Os (ppb)		†(0.1)	† (1)			9?

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* Values in parenthesis are magnitudes only, not usable values

† Originator's values

Table 14 (cont.)

ppm	AGV-1	BCR-1	DTS-1	G-2	GSP-1	PCC-1
Pb	33	14	11	30	54	11
Pd (ppb)		†(12)	† (1)			5?
Pr	† (7)	7?	† (0.006)	19?	†(50)	
Pt (ppb)	† (1)	†(2)	† (3)			10?
Ra (ppt)	† 0.7?	† 0.6?	† 0.0013?	† 0.7?	† 0.7?	† 0.0018?
Rb	67	47	0.05?	170	250	0.3?
Re (ppb)		† 0.8?				† 0.07?
Rh (ppb)		† 0.2?	† 0.9?			† 1?
Ru (ppb)		†(1)	† (2.5)			† 9.5?
Sb	4.3?	0.6	0.5?	0.06?	3.1?	1.4?
Sc	12.5	33	3.8	3.5	6.6	9?
Se		0.1?				
Sm	5.9	6.5	† (0.004)	7.2	25?	† (0.008)
Sn	3.6	2.5	1.7?	1.4?	5?	1.6?
Sr	660	330	0.4?	480	240	0.4
Ta	1.4?	0.8?		0.8?	1?	
Tb	0.7?	1.0	† (0.0003)	0.5?	1.4?	† (0.001)
Th	6.4	6.1	† (0.01)	25	105	† (0.01)
Tl	1.6?	0.3?	† (0.0005)	1.2?	1.3?	† (0.0008)
Tm		0.6?	† (0.001)			
U	1.95	1.7	0.004?	2.1	2.1	0.005?
V	125	420	11	36	54	29
W	† (0.55)	0.4?	† (0.04)	† (0.1)	† (0.1)	† (0.06)
Y	19	40	† (0.05)	11	29	
Yb	1.9	3.4	† (0.01)	0.86	1.9	† (0.02)
Zn	86	125	46	84	105	41
Zr	230	185	(10)	300	500	† (7)

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* Values in parenthesis are magnitudes only, not usable values

† Originator's values

USGS III

The eight samples in this set seem to have been prepared and analyzed over an appreciable period of time. Although some analytical data on some of the samples appeared in the literature as early as 1966 (Johansen and Steinnes, 1966; Brunfelt and Steinnes, 1966), the first reasonably comprehensive report did not appear until 1976 (Flanagan, 1976a), and that report contained no information later than 1972. Our own laboratories made major contributions of analytical data for these samples.

The samples may be described as follows:

BHVO-1 is a "basaltic lava from Kilauea caldera, Kilauea volcano, Hawaii". Geological background information and some analytical data were given by Flanagan et al. (1976).

MAG-1 is "a fine-grained gray-brown clayey mud from the Wilkinson Basin of the Gulf of Maine". More detailed information and analytical data may be found in Manheim et al. (1976)

QLO-1, a quartz latite (dellenite), was described by Walker et al. (1976) as "...a sample of dense black volcanic rock...collected in Lake County, Ore...". Analytical data were also supplied.

RGM-1 was described by Tatlock et al. (1976) as a "rhyolite from Glass Mountain, Siskiyu County, Calif.... selected...because it is a glass and is therefore less subject to the phase heterogeneities... in a crystalline rock". The same reference provided a limited quantity of analytical data.

SCo-1, a Cody shale from Natrona County, Wyoming, was described by Schultz et al. (1976) as "a medium dark-gray (Munsell N-4) silty shale having thin lighter colored silty laminations". Limited analytical data were provided in the reference.

SDC-1, according to Flanagan and Carroll (1976), is "a dark-grey pervasively foliated muscovite-quartz schist with a homogeneous thinly streaked texture..." from Rock Creek Park, in Washington, D.C.

SGR-1 was referred to by Flanagan (1976a, p.4) as an "oil shale from the Mahogany zone of the Green River Formation...". Little further information was supplied for this sample, although some analytical data were reported in a few of the other papers in Flanagan (1976a).

STM-1, the subject of the paper by Snavely et al. (1976), is a "peralkaline nepheline syenite", from the Georgia-Pacific quarry under Table Mountain, Oregon. Some analytical data were provided in the reference.

Careful study of Flanagan (1976a) suggests that the samples making up USGS III were not processed in as co-ordinated a manner as were those of USGS II. For only three of the samples, the descriptive papers included duplicate classical analyses for major and minor constituents (done by two separate analysts) and d.c.-arc spectrographic analyses for many trace elements, reported by three different USGS laboratories. For four others, the descriptive papers gave varied analytical coverage, including the use of a variety of analytical techniques, some of which were applied to only one, or a small number of constituents. The eigth sample, SGR-1, the "oil shale" and therefore the most unusual of all, was not described in a separate paper. Eighteen other papers in Flanagan (1976a) reported data on anywhere from one to many constituents in anywhere from one to all eight of the samples, obtained by a variety of analytical techniques, emanating from USGS laboratories and from a number of other institutions.

Major emphasis in the data reported on the USGS III samples appears to have been on the use of analysis of variance as a means of assessing the degree of inter-bottle inhomogeneity. Although many of the papers in Flanagan (1976a) were directed to that goal, the manner of presentation of the data was far from consistent. There was no systematic tabulation of all available results for each constituent of each sample of this group, in the manner done in earlier compilations on USGS I and II (Flanagan, 1969, 1976c; Fleischer, 1965, 1969). Nowhere in Flanagan (1976a) was there any attempt to assign probable values of the concentrations of the constituents in the eight samples. As of early 1982, the USGS had not published any "best values" for USGS III.

Systematic analysis for many constituents of this set of samples was done in GSC laboratories on replicate portions out of separate bottles, shortly after publication of U.S. Geological Survey Professional Paper 840. In addition, through the kindness of K. Govindaraju, we were provided with the results obtained on USGS III in the laboratories of the Centre de Recherches Pétrographiques et Géochimiques (CRPG) and the laboratories of l'Université de Nancy, Nancy, France. However, even after combining the GSC and CRPG results with those scattered in the various papers in Flanagan (1976a), there were still insufficient numbers of results to apply the select laboratories method for deducing usable values. Median values of all results for each constituent of each sample were therefore listed in Abbey (1977b and 1980), with question marks.

Eventually, Gladney and Goode (1981) compiled nearly all reported results on these samples that had appeared in the literature. After using both statistical and subjective considerations to eliminate outliers, they calculated mean values and "uncertainties" (standard deviations) for many constituents of all eight samples.

Although the work of Gladney and Goode was a valuable contribution, there were reasons to question the validity of their derived values. To their credit, they emphasized that their values were "mere averages, nothing more". However, in a later paper, Gladney (1981) implied that such "mere averages" – in that case on the CCRMP rocks – were as good measures of "best values" as were the usable values derived by the select laboratories method (Abbey, 1979).

The most serious objection to the work of Gladney and Goode was their working with only results that had appeared in the literature. Other errors included the combination of results by two or more different analysts as a single value (merely because all had been done at about the same time in USGS laboratories), failure to distinguish carbonate from non-carbonate carbon, and failure to distinguish "as received" determinations from those reported on the dry basis.

It was therefore decided to attempt a re-evaluation of USGS III at the Geological Survey of Canada, using the select laboratories method.

For that purpose, the compilation of Gladney and Goode was combined with our own results, with those from Nancy, and with additional data obtained from the literature and by private communication. Repeated requests to the U.S. Geological Survey for unpublished results reported by their own and other laboratories elicited no additional figures. In any event, the GSC evaluation used nearly twice as much raw data as did that by Gladney and Goode (1981).

Results of the re-evaluation are given in Table 15, more details in Abbey (1982a), where the values are also compared with those of Gladney and Goode. The unusually large number of values with question marks in Table 15 is due to the limited quantity of raw data – even after including the additional results over and above the compilation of Gladney and Goode (1981). The actual total number of individual reported results used to evaluate all eight samples of USGS III was far less than those available for the evaluation of merely three samples of CCRMP rocks shown in Table 9.

For five of the eight samples in Table 15, both totals and iron-oxide compatibilities are within acceptable limits. The three exceptions were the samples with relatively high organic contents – the marine mud and the two shales. Perhaps more thorough analysis for individual organic constituents would improve the totals for those three samples – as the availability of more analytical data for all constituents might serve to reduce the number of "question-marked" values.

Some time after completion of the work leading to the values in Table 15, two other items appeared concerning USGS III. Kennedy et al. (1981) reported a "complete" analysis of the eight samples, mainly by methods based on x-ray fluorescence. Their data were, in general, of good quality, and would have made a useful addition to the other raw data used in the evaluation, had they appeared earlier. In a somewhat different case, Steinnes (1981), on behalf of the International Union of Pure and Applied Chemistry (IUPAC) Commission on Analytical Radiochemistry and Nuclear Materials, published a set of estimated compositions for these samples, based on Flanagan (1976a), on some of his own unpublished data and on five other reports, all of which were already included in the compilation of Gladney and Goode (1981). Steinnes emphasized that his figures were "...given only to indicate the elemental composition of the samples.... not to be considered as recommended values".

USGS IV

Background information on these three samples was provided by Flanagan and Gottfried (1978).

BIR-1 is a basalt from southwestern Iceland, provided by the Nordic Volcanological Institute, Reykjavik, and intended as a replacement for BCR-1.

DNC-1 is a diabase (dolerite), from near Durham, North Carolina, provided by the Geology Department, University of North Carolina, "...the sample may be regarded as a very primitive continental tholeiite" (Flanagan and Gottfried, 1978).

W-2 is a diabase, intended as a replacement for the long-exhausted W-1. It was collected near Centreville, Virginia, at the Bull Run (later Luck) Quarry.

Although the samples were distributed to collaborating analysts in mid-1978, neither a compilation of data nor a set of "best values" had appeared three-and-a-half years later.

Table 15. USGS III – usable values (compiler's)

Per cent (dry basis)	Basalt BHVO-1	Marine Mud MAG-1	Quartz Latite QLO-1	Rhyolite RGM-1
SiO_2	49.90	51.19?	65.93	73.47
TiO_2	2.69	0.75	0.62	0.27
Al_2O_3	13.85	16.46	16.37	13.80
Fe_2O_3	2.74?	*	0.98?	0.50?
FeO	8.55?	*	2.98?	1.24?
MnO	0.17	0.10	0.09	0.04
MgO	7.31	3.13	1.04	0.28
CaO	11.33	1.38	3.24	1.15
Na_2O	2.29	3.91	4.23	4.12
K_2O	0.54	3.72	3.63	4.35
H_2O^+	0.20?	5.8?	0.34?	0.50?
CO_2	0.04?	?	0.01?	0.01?
L.O.I.		?		
P_2O_5	0.28	0.18?	0.26	0.05?
F	0.038?	0.09?	0.028?	0.034?
S	0.011?	0.43?	0.004?	0.01?
Others	0.26?	5.43?	0.29?	0.23?
Sum	100.20?	99.55?	100.04?	100.05?
O/F, S, Cl	0.02?	0.95?	0.02?	0.03?
Sum (corr.)	100.18?	98.60?	100.02?	100.02?
Fe_2O_3TR	12.23	6.98	4.29	1.89
Fe_2O_3TC	12.24?	*	4.29?	1.88?
ppm				
Ag	0.056?			0.1?
B		130?	37?	31?
Ba	135	480	1400	800
Be		3?	2?	2.5?
Bi	0.014?			0.3?
†C (pct)		2.2?		
Cd		0.2?		
Ce	39	86?	59?	48?
Cl	94?	3.09?(pct)	220?	540
Co	45	20	7.4	2.3?
Cr	300	105	4.2?	4?
Cs	0.15?	8.6?	1.7?	
Cu	140	27	27	11
Dy	5?			
Eu	2.0	1.5?	1.5?	0.7?
Ga	21?	21?	18?	15?
Gd	6.0	6.6?	4.7?	
Hf	4.3	3.6?	4.6?	6.0?
La	17?	41?	27?	23?
Li	4?	78?	23?	50?
Mo	1?	1?	2.6?	2.3?
Nb	19	9.6?	10.5?	9.4?
Nd	24	41	23?	19?
Ni	120	54	5.5?	6?
Pb		24?	21?	21?
Rb	10	150	74	155?
Sb	0.17?	1?	2?	1.3?
Sc	31	17	9?	4.7
Sm	6.1	8.1?	5.1?	4.3?
Sn		5.2?		
Sr	420	140	350	100
Ta	1.1?	1.1?	0.9?	1.0?
Tb	1.0?	1.0?	0.75?	
Th	1.0	12.5?	4.8?	15?
Tm	0.3?			
U	0.4?	2.8?	2.0?	5.8?
V	320?	140	61	14?
W				1.6?
Y	27?	27?	24?	25?
Yb	1.9	2.6	2.5	2.5
Zn	105	135	64	36
Zr	180	130	175	200

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† Non-carbonate carbon.

* Accurate Fe", Fe‴ determinations precluded by high organic content

Table 15 (cont.)

Per cent (dry basis)	Shale SCo-1	Mica Schist SDC-1	Shale SGR-1	Syenite STM-1
SiO_2	63.39	66.15	28.30	59.66
TiO_2	0.62	1.00	0.24	0.13
Al_2O_3	13.70	15.75	6.49	18.44
Fe_2O_3	4.26?	2.46?	*	2.89?
FeO	0.86?	3.98?	*	2.10?
MnO	0.05	0.12	0.032	0.22
MgO	2.76	1.70	4.57	0.10
CaO	2.64	1.39	8.32	1.09?
Na_2O	0.95	2.10	3.02	8.95
K_2O	2.82	3.24	1.63	4.29
H_2O^+	3.90?	1.70?	‡	1.44?
CO_2	2.75?	0.09?	‡	0.02?
L.O.I.			41.6?	
P_2O_5	0.22?	0.18	0.29?	0.16
F	0.077?	0.062?	0.19?	0.091?
S	0.066?	0.067?	1.56?	?
Others	0.45?	0.23?	0.18?	0.52?
Sum	99.51?	100.22?	99.30?	100.10?
O/F, S, Cl	0.07?	0.06?	0.86?	0.05?
Sum (corr.)	99.44?	100.16?	98.44?	100.05?
Fe_2O_3TR	5.22	6.85	2.98	5.20
Fe_2O_3TC	5.22?	6.88?	*	5.22?
ppm				
Ag		0.5?		0.08?
As	15?		63?	
B	66?		50?	
Ba	590	650	290	560
Be	1.7?	3?		9?
†C (pct)	0.24?			
Ce	63	92	38?	260
Cl	51?	35?	50?	450?
Co	11	17	12.5?	1?
Cr	71?	66?	33?	4?
Cs	7.8?	3.9?	5.3?	1.5?
Cu	28	28	65	4?
Dy	4.2?			
Er	2.5?			
Eu	1.2?	1.7?	0.54?	3.7
Ga	14?	22?	8.6?	37?
Gd	4.2?	7.2?		10?
Hf	4.3?	8.1?	1.4?	27?
Ho	0.9?			2?
La	29?	42?	20?	150
Li	44?	32?		30?
Mo	1.4?		36?	5.2
Nb	10?	18.5?	5.3?	270?
Nd	27	38	15	78
Ni	30	36	34	3?
Pb	28?	23?	41?	18?
Rb	115	120?	81?	120?
Sb	2.5?	0.54?	3.5?	1.7?
Sc	11?	15?	5?	0.7?
Se			3.4?	
Sm	5.1?	8.3?	2.8?	13
Sn	3.7?			9?
Sr	170	180	430	700
Ta	0.9?	1.3?	0.5?	18?
Tb	0.8?	1.2?	0.35?	1.6?
Th	9.6?	12?	4.9?	31?
Tm	0.5?	0.7?		
U	2.9?	3.0?	5.4?	9.1?
V	135?	105?	125	
W		0.8?		3.8?
Y	24?	42?	13?	46?
Yb	2.2	4.2	1.0	4.3
Zn	105	105	81	240
Zr	135	300?	55?	1300

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* Accurate Fe", Fe‴ determinations precluded by high organic content.

† Non-carbonate carbon. ‡ High petroleum content interfered.

However, through the kindness of F.J. Flanagan, this author was provided with estimates of the best values of a number of constituents, as shown in Table 16. Flanagan's values have been converted to the dry basis, using his "best values" of H_2O^-. Some of his trace-element values have been rounded to render them more consistent with other figures in this paper.

As far as is known, Flanagan's values are based on arithmetic averages of reported results (including those from GSC) after elimination of outliers by a combination of statistical and subjective considerations. In some cases, particularly where few results were available, "best values" were based entirely on subjective judgement. The limited number of results for some constituents is clearly indicated by the large number of question marks in Table 16. It is also noteworthy that the summations - particularly for DNC-1 and W-2 - are somewhat high. A similarly high summation occurs with W-1 (Table 13), where values were also provided by the originators. Are the discrepancies related to the nature of the diabase samples, or are they the result of the derivation procedure? A possible support for the latter alternative may be drawn from the fact that values derived by the select laboratories method for two samples of compositions similar to those of DNC-1, W-1 and W-2, namely MRG-1 (Table 9) and BCR-1 (Table 14) gave noticeably better summations.

Nevertheless, these three samples should prove valuable additions to the geoanalyst's working tools. In particular, the relatively low concentrations of certain common trace elements in BIR-1 will likely be useful. One hopes that later evaluations, based on more analytical raw data, will enhance the value of these samples.

Other USGS Materials

It is known that the U.S. Geological Survey has prepared several additional rock materials for use as reference samples, including DTS-2 (a replacement for DTS-1), BBM-1 (a basalt), GSM-1 (a gabbro), TLM-1 (a tonalite) and SDo-1 (a shale), but little information has appeared in print.

It should be noted that the designation SDo-1 duplicates that of a terrigene clay from the USSR. Because so little information is available on both samples, no effort was made in this work to assign distinguishing designations.

Myers et al. (1976) published results and median values for certain trace elements, as determined by various laboratories, in four synthetic glasses of rock-like composition, GSB, GSC, GSD and GSE. Although a number of laboratories in institutions other than the USGS (including the GSC Spectrographic Laboratory) participated in the collaborative analysis, the samples are not available for general distribution. Their compositions are therefore not given in this paper.

The U.S. Geological Survey has also prepared two reference samples of manganese nodules, one from the Atlantic Ocean, the other from the Pacific. They were described in some detail by Flanagan and Gottfried (1980). Methods used in their analysis in the USGS laboratories were outlined by Neil (1980). Because the compositions of the manganese nodules are so far removed from those of silicate rocks, the samples are not listed in this paper. However, those who may find them useful will find all available information in the two references mentioned above.

Table 16. USGS IV – usable values (originator's)

Per cent (dry basis)	Basalt BIR-1	Diabase DNC-1	Diabase W-2
SiO_2	48.00	47.29	52.81
TiO_2	0.96	0.49	1.06
Al_2O_3	15.54	18.39	15.49
Fe_2O_3	2.06?	1.80?	1.65?
FeO	8.35?	7.34?	8.36?
MnO	0.175	0.148	0.167
MgO	9.71	10.16	6.39
CaO	13.33	11.52	10.89
Na_2O	1.82	1.89	2.21
K_2O	0.03	0.23	0.63
H_2O^+	0.016?	0.73?	0.55?
CO_2	?	?	?
P_2O_5	0.021?	0.07?	0.14
F	?	?	?
S	?	?	?
Others	0.18?	0.35?	0.15?
Sum	100.15?	100.41?	100.50?
O/F, S	0.00?	0.00?	0.00?
Sum (corr.)	100.15?	100.41?	100.50?
Fe_2O_3TR	11.30	10.00	10.86
Fe_2O_3TC	11.34?	9.96?	10.94?
ppm			
As			1.2?
Ba	6.1?	120	175
Be		0.95?	
Ce	1.6?	9.1?	23
Co	52	57	43
Cr	370?	270?	92
Cs			1.0?
Cu	125?	100?	105
Dy	3.7?	3.0?	
Eu	0.55?	0.59?	1.1
Ga	15?	15?	16?
Hf	0.65?	1.0?	2.6?
La	0.65?	3.6?	10.5
Li	3.6?	5.2?	9.6?
Lu	0.29?	0.32?	0.33?
Nb	2.3?	3.2?	6.8?
Nd		5.2?	13.5?
Ni	165?	250	70
Rb		4.7?	21
Sb	0.5?	1.0?	0.85?
Sc	43?	31	36?
Sm	1.0?	1.4?	3.3?
Sr	105?	145?	190?
Ta			0.5?
Tb		0.4?	0.65?
Th			2.4?
Tm		0.3?	0.4?
V	310	150	260
Y	16?	18?	23?
Yb	1.7?	2.0?	2.1
Zn	70?	70	80
Zr	18?	38?	100?

USGS-AEG – U.S. GEOLOGICAL SURVEY and ASSOCIATION OF EXPLORATION GEOCHEMISTS

(Contact: Glenn H. Alcott, U.S. Geological Survey, Box 25046, MS 973, Federal Center, Denver, CO 80225, U.S.A.).

Six samples have been prepared for use as reference materials in geochemical exploration. They represent a variety of compositions, some of which are close to those of silicate rocks. They were described by Allcott (personal communication) as follows:

GXR-1: Jasperoid from Drum Mountains, Utah.
GXR-2: Soil (0-18 cm depth) from Park City, Utah
GXR-3: Fe-Mn-W-rich hot spring deposit from Humboldt Country, Nevada.
GXR-4: Porphyry copper mill heads, provided by a mining company in Utah.
GXR-5: Soil (B horizon, 7.5-25 cm depth) from Somerset County, Maine.
GXR-6: Soil (B horizon, 15-45 cm depth) from Davidson County, North Carolina.

Gladney et al. (1979), having observed the wide scatter of results obtained in USGS "in house" and "round robin" analyses, attempted to resolve the discrepancies by undertaking repeat analyses, using a variety of analytical techniques, although they relied heavily on neutron-activation methods for most trace elements. Largely on the basis of their own results, Gladney et al. then listed recommended values for a variable number of constituents of all six samples. Because of the inevitability of interlaboratory bias, it is difficult to accept the results from one laboratory as a firm basis for recommended values, particularly where only one analytical method was used. Some of the values for the GXR samples listed in Table 17 must therefore regarded with some reservation and used with caution. Question marks have been added (a) where Gladney et al. (1979) did not recommend a value, but listed sufficient results in their compilation to qualify their median as a first approximation (as used in the select laboratories method), and (b) to values for all silica and high alumina and total iron oxide values recommended by Gladney et al. where the magnitude of their "uncertainty" suggested such action. Some of the trace-element values have been rounded to render them more compatible with others listed in the Tables.

The low summations on all six samples are evidently the result of the absence of data on such constituents as water, carbon dioxide, phosphorus, sulphur and fluorine. One or more of those constituents may well be major components of some of the samples, notably GXR-3.

The compilation of Gladney et al. (1979) gave no indication whether the listed data were on the "as received" or "as dried" basis. Inasmuch as the samples are intended for use in geochemical exploration, only the trace elements are likely to be of major interest; no H_2O^- values were apparently reported. The values for all constituents are therefore listed in Table 17 on an "as reported" basis. It is possible that some of the samples may have significant moisture contents.

NBS – NATIONAL BUREAU OF STANDARDS (U.S.A.)

(Contact: Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234, U.S.A.)

The National Bureau of Standards is one of the oldest, largest and most respected of the world's producers of reference materials. As it comes under the jurisdiction of the Department of Commerce, the Bureau has concentrated its production of "Certified Chemical Composition Standards" on materials required by industry. A majority of the products in that area have been metals and alloys, but among the many other materials involved has been a small group of ores, minerals, refractories and glasses, some of which may prove useful in the analysis of rocks. Recently, NBS has introduced two reference samples of actual rocks.

Evaluation of most NBS materials has been based on the "in-house" method, which may be the reason why the number of elements for which firm usable values are available in each sample is generally limited. For purposes of this work, attention is concentrated on some 15 NBS samples, arbitrarily selected because of their possible usefulness in rock analysis. They are examined in three groups: (1) two rocks, two feldspars and two clays; (2) three bauxites, two sands and a glass; and (3) two fly ashes and a river sediment.

In the compositional tables for NBS samples, it will be noticed that some trace elements are expressed to more significant figures than are usual in the rest of this work. Such additional figures are used only with values designated by NBS as "certified" and represent this author's recognition of the authoritative nature of NBS Certificates.

Rocks and minerals

The two rock samples are an obsidian, NBS-278, and a basalt, NBS-688. The former was described by Uriano (1981a) as "...a finely powdered obsidian rock, which was obtained from Clear Lake, Newberry Crater, Oregon". In another certificate, Uriano (1981b) described the latter rock as "...a finely powdered basalt rock that was obtained from a Cenozoic basalt flow near Jackpot, Nevada". Both are supplied with "certified values" for a limited number of constituents and a somewhat larger list of "information values", the latter being shown with question marks in Table 18. Certified values were based largely on "in-house" analyses, combined with contributions from Pennsylvania State University, Northern Illinois University and the University of Missouri. (The square brackets around the Fe_2O_3T figures in Table 18 merely indicate that they were not counted in the summation.)

Uriano (1981a) pointed out that NBS-278 is highly hygroscopic and that adsorbed water cannot be driven off at normal drying temperatures. He recommended that the sample be dried to constant weight at temperatures between 350 and 600°C. NBS-688 may be dried at the more usual temperature of 105°C.

The potash feldspar, NBS-70a, and the soda feldspar, NBS-99a (as well as their predecessors, NBS-70 and -99) were for many years the only NBS samples with compositions close to those of common rocks. Two "Certificates of Analysis" (Meinke, 1965a, b) listed values for the two materials as "provisional" but the identical values are shown without restriction in the 1979-80 edition of NBS Special Publication 260, their catalog of standard reference materials. The values are listed in Table 18, but the scanty information on trace-element concentrations severely limits the usefulness of these samples.

The two clay samples are included in this work because their compositions may prove useful in rock analysis. The values listed in Table 18 are from Cali (1969a, b), where it was pointed out that they are based on samples dried two hours at 140°C. Few trace-element values are shown, but at least there are more for these samples than for the two feldspars. The values for most of the constituents are the means of those found in NBS laboratories and in one or two outside establishments.

With both the feldspars and the clays, the elements usually considered as traces in rocks are listed on the NBS certificates as per cent, oxide. The significant figures shown are, in some cases, so few that conversion to parts per

Table 17. USGS-AEG – usable values (Gladney et. al., 1979 – see text)

Per cent	Jasperoid GXR-1	Soil GXR-2	Deposit GXR-3	Copper Mill-head GXR-4	Soil GXR-5	Soil GXR-6
SiO_2	49.2?	49.2?	13.0?	67.0?	42.1?	49.0?
TiO_2	0.11	0.47	0.17	0.43	0.35	0.83
Al_2O_3	6.69?	35.1?	11.7?	14.0	39.3?	31.4?
Fe_2O_3T	35.3?	2.7	26.6?	4.25?	4.56	7.98?
MnO	0.12?	0.12	2.88	0.018	0.036	0.13
MgO	0.35	1.46	1.06	2.74	2.02	1.03
CaO	1.21	1.15	19.7	1.26	1.05	0.14
Na_2O	0.074	0.75	1.05	0.71	1.04	0.14
K_2O	0.064	1.70	0.89?	5.2	0.99	2.46
H_2O^+						
CO_2						
P_2O_5						
F						
S						
Others	0.53?	0.44?	2.70?	1.16?	0.33?	0.29?
Sum	93.65?	93.09?	79.75?	96.76?	91.78?	93.40?
ppm						
As	460	31	4000	98	12	340
B	15.3	44	180	4.3	25	11
Ba	560	2000	4700	1350	1800	1100
Be	1.10	1.65	26	2.1	1.20	1.1
Br	0.39	3.0		0.50	7.8	1.4
Ce	19	50	16	115	40	38
Co	9.3	9	48	16	30	14
Cr	10	37	19	64	100	96
Cs	4	5	200	3	2.2	4.8
Cu	1300	74?	15?	6500	360	105
Dy	3.1	3.3		2.6	2.0	2.8
Eu	0.68	0.8	0.40	1.6	0.94	0.78
Ga	12	32		15	34	30
Hf	1.1	9.6	2.4	8.0	6.2	5.3
Hg	3.9	3.2	0.38	0.13	0.17	0.08
La	6.1	25	8.5	64	18	14
Mo	18?			310	30	1.7
Ni	42	18	55	38	63	22
Pb	670	620	15		22	110
Rb	29	86	115	175	40	105
Sb	125	48	40	4.4	2	3.8
Sc	1.7	6.8	18	8.3	7.8	31
Se	18.5	0.74	0.22	6.0	1.1	1.05
Sm		3.3	1.0	6	2.9	2.4
Sr	280	160	1150	220	120	42
Ta	0.2	0.76	0.32	0.77	0.46	0.52
Th	2.3	8.3	2.9	22	5.3	5.2
U	35	3.0	3.1	6.4	2.1	1.60
V	88	57	39	92	60	180
W		1.8	10800	28		0.88
Yb	1.8	2.2	0.76	1.8	2.0	2.7
Zn	740	500	220	64	50	120
Zr	66	200		200	140	105

Table 18. NBS rocks and minerals – usable values (originators')

Per cent (dry basis)	Obsidian *NBS-278	Basalt NBS-688	Potash Feldspar NBS -70a	Soda Feldspar NBS-99a	Flint Clay *NBS-97a	Plastic Clay *NBS-98a
SiO_2	73.05	48.4	67.1	65.2	43.67	48.94
TiO_2	0.245	1.17	0.01	0.007	1.90	1.61
Al_2O_3	14.15	17.36	17.9	20.5	38.79	33.19
Fe_2O_3T	*[2.04]	[10.35]	0.075	0.065	0.45	1.34
Fe_2O_3	0.53	1.86				
FeO	1.36	7.64				
MnO	0.052	0.167				
MgO	0.23?	8.4?		0.02	0.15	0.42
CaO	0.983	12.17?	0.11	2.14	0.11	0.31
Na_2O	4.84	2.15	2.55	6.2	0.037	0.082
K_2O	4.16	0.187	11.8	5.2	0.50	1.04
CO_2	0.01?	0.05?				
L.O.I.			0.40	0.26	13.32	12.44
P_2O_5	0.036	0.134		0.02	0.36	0.11
F	0.05?	0.02?				
Others	0.22?	0.19?	0.08?	0.26?	0.45?	0.21?
Sum	99.92?	99.89?	100.03?	99.87?	99.74?	99.70?
O/F, etc.	0.02?	0.01?	0.00?	0.00?	0.00?	0.00?
Sum (corr.)	99.90?	99.88?	100.03?	99.87?	99.74?	99.70?
ppm						
B	25?					
Ba	1150?	200?	180?	2300	670	300?
C (non-$CO_3^=$)	470?					
Ce	62?	13?				
Co	1.5?	50?				
Cr	6.1?	330			200?	200?
Cs	5.5?					
Cu	5.9	96?				
Eu	0.85?	1.1?				
Gd	5.3?					
Hf	8.4?	1.6?				
Li					500?	330
Lu	0.75?	0.34?				
Ni	3.6	150?				
Pb	16	3.3				
Rb	128	1.9	550?			
Sb	1.5?					
Sc	5.1?	38?				
Sm	5.7?	2.8?				
Sr	63.5	169			1500	330
Ta	1.2?					
Tb	1.0?	0.45?				
Th	12	0.3				
Tl	0.54					
U	4.6	0.37?				
V		250?				
Yb	4.5?	2.1?				
Zn	55?	58?				
Zr					470?	310?

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* Notes

Values in square brackets not included in totals.
NBS-278 dried at 350-360°C, NBS-97a and -98a dried at 140°C.

Table 19. NBS bauxites, sands and a glass – usable values (originator's)

Per cent (dry basis)	Bauxite NBS-69b	Bauxite NBS-696	Bauxite NBS-697	Glass sand NBS-81a	Glass sand NBS-165a	Opal Glass NBS-91
SiO_2	13.4	3.80	6.80	*(99+)	(99+)	67.53
TiO_2	2.0	2.7	2.6	0.12	0.011	0.019
Al_2O_3	49.3	54.7	45.7	0.66	0.059	6.01
Fe_2O_3T	7.1	8.7	20.0	0.082	0.012	0.081
MnO	0.09	0.003	0.35			0.008?
MgO		0.01	0.17			0.008?
CaO	0.12	0.01	0.60			10.48
Na_2O	0.03	0.02	0.046			8.48
K_2O	0.80	0.01	0.07			3.25
L.O.I.	27.22	29.88	22.2			* 0.50?
P_2O_5	0.12	0.06	0.90			0.022
F						5.72
SO_3	0.63	0.24	0.15			
Others	0.04?	0.12?	0.22?			0.38?
Sum	100.85?	100.25?	99.80?			102.49?
O/F,etc.	0.00?	0.00?	0.00?			2.41?
Sum (corr.)	100.85?	100.25?	99.80?	Incomplete		100.08?
ppm						
As						1350
Ba		45?	80?			
Cl						140
Cr	70?	310	680?	31	0.8?	
Pb						900
V	170?	390?	390?			
Zn	24?	16?	320?			640?
Zr				250	44?	70

* Notes:

Values in parentheses are magnitudes only, not usable values
L.O.I. on NBS-91 based on ignition at about 875°C.

million, (element), can lead to some uncertainty. For example, 0.02 per cent BaO is equivalent to about 180 ppm Ba, but only if the 0.02 per cent is actually at least 0.020. The converted values are therefore shown with question marks where such uncertainty exists.

Bauxites, sands and glass

The three bauxites shown in Table 19 were among the "non-rock" NBS samples selected arbitrarily for their possible usefulness in calibrations because of the relatively low silica and high alumina contents. They may also be combined with ANRT-BX-N or BCS-395 to make a convenient set of four or five. Alternatively, they may be combined with other NBS bauxites not included in this compilation. In any event, it must be remembered that bauxites may behave differently than would silicate rocks in certain analytical operations.

The values shown in Table 19 for NBS-69b, -696, and -697 are from NBS Special Publication 260, 1979-80 Edition. The apparently high summation for NBS-69b could conceivably be due to the presence of some ferrous iron, but that appears unlikely, particularly since NBS-697, with the highest total iron content of the three, has a low summation.

The two glass sands, NBS-81a and -165a, were prepared in co-operation with the American Society for Testing Materials, and evaluated by means of round-robin analyses (Cali, 1978a, b). The very limited number of constituents for which values have been established restricts the usefulness of these samples, but they may find application in the analysis of other silica-rich materials, perhaps in combination with such samples as BCS-267 and -313.

NBS-91, one of the oldest samples still available, was selected from the various NBS glasses because its composition is closer to those of typical rocks than are those of any of the other glasses. The high fluorine content, which may be useful in analytical applications, can be a source of difficulty in determining loss on ignition (Burgess, 1931). The 0.50 per cent loss, shown with a question mark in Table 19, was reportedly obtained by heating "...for one hour just below the temperature of fusion (about 875°C)...". Further heating at higher temperatures resulted in larger losses, probably in the form of silicon tetrafluoride.

The evaluation was based on collaborative analysis involving five laboratories, each listed value being a mean of reported results, after rejection of a few conspicuous outliers.

Fly ashes and river sediment

NBS-1633, -1633a and -1645 were selected from the NBS environmental materials because of their compositional similarity to silicate rocks.

Although the three samples were intended for use primarily in environmental studies, all of them contain many trace elements of geochemical interest. The older of the two fly ash samples, NBS-1633, has had a rather checkered history. For one thing, it was apparently prepared in insufficient quantity. Although first released in March 1975 (Cali, 1975), NBS-1633 was no longer listed in the 1979-80 edition of the NBS catalog. A replacement, NBS-1633a, was mentioned there as "in preparation".

Before the NBS certificate appeared, Lehmden et al. (1974) published the results of a nine-laboratory collaborative analysis of NBS-1633 and several related samples, their main concern apparently being a comparison of the relative merits of the various analytical techniques used. Shortly after initial release of NBS-1633, Ondov et al. (1975) reported results of a similar study, involving four laboratories, using mainly nuclear analytical techniques. They listed "average concentrations", with uncertainties, for more than twice as many constituents as were listed on the certificate.

Earlier papers in this series (Abbey, 1977b, 1980) listed unquestioned values taken from the certificate (Cali, 1975). For constituents not shown on the certificate, the values of Ondov et al. were listed, but with question marks.

A major contribution to the evaluation of a number of NBS environmental reference materials appeared in the work of Gladney (1980), who compiled large quantities of data from the literature and calculated average values, with uncertainties, after elimination of certain outliers. Although the relatively large quantity of data for NBS-1633 in Gladney's compilation suggested that good values could be computed for more constituents than those listed on the NBS certificate, there was some hesitation at accepting his trimmed means as usable values, as there was with the values of Gladney and Goode (1981) for USGS III.

It was therefore decided to derive a new set of values from Gladney's (1980) compilation, but using the select laboratories method. In Table 20, the values shown with asterisks are from the NBS certificate (Cali, 1975); those with no mark are "unquestioned" values, derived by the select laboratories method; those with question marks include some that would be so designated by the select laboratories method and some given as "information" values on the certificate. Generally, NBS certificate values were given precedence, except where the select laboratories method showed that unquestioned values could be attained for constituents for which the certificate showed merely information values.

The replacement material, NBS-1633a, was listed by Gladney (1980), using the values from its NBS certificate. The only additional data gleaned from the literature by Gladney were all apparently from a single source. The values listed for this sample in Table 20 are based on Gladney's listing of "certified and non-certified" concentrations, the former indicated with asterisks, the latter with question marks. (Some confusion inevitably arose from Gladney's repeated use of the term "elemental concentrations" in his various tables, thereby obscuring the important difference between individual reported values and consensus values, derived from a number of reported values, by whatever method.)

The third material in Table 20, River Sediment NBS-1645, is shown in the same manner as is NBS-1633a. The values are from the certificate (Cali, 1978c).

The low summations for all three materials in Table 20 suggest that other constituents are present than those actually listed. With NBS-1645, the sample most like an actual rock, the total is closer to 100 per cent than it is with either of the two fly ashes, and the certificate lists two additional "constituents": "oil and grease" and "chemical oxygen demand". Unfortunately, neither of those can be expressed in a form which can be meaningfully added to the total.

No similar additional constituents are mentioned for the fly ash samples, but it is conceivable that they may contain some unburned carbon.

Table 20. NBS fly ashes and river sediment – usable values (see text for sources)

Per cent (dry basis)	Fly ash NBS-1633	Fly ash NBS-1633a	River sediment NBS-1645
SiO_2	(45)	48.8*	(51)
TiO_2	1.21	1.33?	
Al_2O_3	23.58	(26)	4.0?
Fe_2O_3T	8.91	13.4*	16.2*
MnO	0.064*	0.025?	0.101*
MgO	2.79	0.755*	4.0?
CaO	6.56	1.55*	4.0?
Na_2O	0.42	0.23*	0.74?
K_2O	2.00	2.26*	1.4?
L.O.I.			10.72?
P_2O_5			0.12?
S	0.006?		
Others	0.70?	0.49?	4.66?
Sum	91.24?	94.84?	96.94?
O/F,S,Cl etc.	0.00?	0.00?	0.00?
Sum (corr.)	91.24?	94.84?	96.94?
ppm			
As	61*	145*	66?
Ba	2600	1500?	
Be	12?*	12?	
Br	11		
Cd	1.45*	1.0*	10.2*
Ce	150	180?	
Cl	40?		
Co	40	46?	8?
Cr	131*	196*	2.96(per cent)*
Cs	8	11?	
Cu	128*	118*	109*
Dy	9?		
Eu	2.5?	4?	
Ga	40?	58?	
Hf	8?	7.6?	
Hg	0.14*	0.0023?	1.1*
I	3?		
In	0.28?		
La	82		9?
Lu	1?		
Mo	23?	29?	
N			797*
Nd	62?		
Ni	98*	127*	45.8*
Pb	70*	72.4*	714*
Rb	115	131*	
Sb	7	7?	51?
Sc	27	40?	2?
Se	9.4*	10.3*	
Sm	12		
Sn	10?		
Sr	1400	830*	
Ta	2?		
Tb	2?		
Th	24?*	24.7*	1.62*
Tl	4?*	5.7*	1.44*
U	11.6*	10.2*	1.11*
V	214*	300?	23.5*
W	4		
Y	66?		
Yb	7?		
Zn	210*	220*	1720*
Zr	310?		

* NBS "certified" (or approximate ?*) values

Other NBS materials

NBS Special Publication 260 lists a number of other materials that may prove useful as reference materials for rock analysis, in addition to those selected arbitrarily and shown in Tables 19 and 20. Among them are environmental materials, ores, minerals, refractories, glasses and cements.

NBS also offers some "Trace Element Standards". Of those, feldspar 607 is certified only for rubidium and strontium, presumably for use in geochronology. Glass samples 610 to 617 inclusive have been spiked with some 36 trace elements but certified values have been established for only four to eight elements per sample. There is also the disadvantage in the fact that one sample contains the maximum concentration of all the trace elements, whereas the others appear to be mere dilutions with the "pure" base materials. Inter-element interference effects are more difficult to observe with such series of reference materials. Further, the samples are available only as wafers, one or three millimetres thick. They therefore appear to be of interest only in special techniques which can use samples in that shape.

NBS has also issued a set of "mineral glasses for microanalysis", mainly for use in microbeam analysis for certain major constituents.

As was the case with NBS-1633, there appears to be a rapid turnover of some NBS samples. Some of those listed in this paper are known to be no longer available; new ones may have become available by the time this work is published. The frequently revised NBS catalog lists compositions of current samples only. Users of older samples must therefore carefully guard their original certificates or maintain a continuing file of old catalogs.

BCS – BRITISH CHEMICAL STANDARDS

(Contact: Bureau of Analysed Samples Ltd., Newham Hall, Newby, Middlesbrough, Cleveland TS8 9EA, England).

In terms of the production of reference materials, the Bureau of Analysed Samples may be regarded as the British counterpart of the U.S. National Bureau of Standards. Their "British Chemical Standards" include a variety of samples of many different types, mainly those intended for industrial applications. Some of them are also recognized as "Eurostandards", in collaboration with several continental European countries.

Of the non-metallic materials available from this source, eight have been selected for inclusion in this compilation. They have been divided into two groups: (1) two feldspars, a sillimanite and a bauxite; (2) an iron ore, a slag, a silica brick and a "pure" silica. The choice was more or less arbitrary, assuming that the selected samples are potentially useful in rock analysis. Several other BCS samples may also be suitable; all are listed in their Catalogue 477, dated March 1979.

Unlike its American counterpart, the Bureau of Analysed Samples depends mainly on a consensus approach in evaluating its samples. Collaborative analyses are done by a small group (generally eight to ten) laboratories, located in British industries or in such industrially-oriented institutions as the British Ceramic Research Association. The laboratories are generally those with extensive experience in the analysis of the type of material at hand, and in most cases, their work involves the use of a variety of methods. Results tend to be in good accord; there is therefore little hesitation in accepting their arithmetic means (after rejection of a few very rare outliers) as usable values.

Table 21. BCS feldspars, sillimanite and bauxite – usable values (originators')

Per cent (dry basis)	Soda feldspar BCS-375	Potash feldspar BCS-376	Silli-manite BCS-309	Bauxite BCS-395
SiO_2	67.1	67.1	34.1	1.24
TiO_2	0.38	< 0.02	1.93	1.93
Al_2O_3	19.8	17.7	61.1	52.4
Fe_2O_3T	0.12	0.10	1.53	16.3
MnO	0.003	0.002	0.03?	0.006
MgO	0.05	0.03	0.17	0.02
CaO	0.89	0.54	0.34	0.05
Na_2O	10.4	2.83	0.34	0.03?
K_2O	0.78	11.2	0.46	0.02?
L.O.I.	0.39?	0.35?	0.10	27.8
Others	0.07?	0.12?	0.01?	0.07
Sum	99.98?	99.98?	100.11?	99.87?
ppm				
Ba	90?	450?		
Co	7?			
Cr	25			450
Cs		50?		
Cu	3	5		20
Ga	40?	70?		
Li	70?	20?	50?	
Ni	< 5	< 4		32
Pb	8	61		28
Rb	48	370		
Sr	64	55		23
Zn	12	5		45
Zr	200?			

For many years, BCS samples suffered from a major handicap in the very limited information on their trace-element contents. Recently, an announcement (British Ceramic Research Association, 1979) suggested that steps were being taken to remedy the situation. Subsequently, a "Supplementary Information" sheet (Bureau of Analysed Samples, 1981) provided values for chromium, copper, manganese, nickel, lead, rubidium, strontium and zinc for five BCS samples, including three of those in this compilation. The same reference mentions a more "detailed report covering this first stage...", suggesting that more values may be expected in the future.

Table 21 gives the compositions of the feldspars, the sillimanite and the bauxite. The values for BCS-375 and BCS-376 (for major and minor constituents) are from Ridsdale (1970a, b) respectively. For the sillimanite, all values are from Ridsdale (1961). The values for major and minor elements in the bauxite are from the catalog (Bureau of Analysed Samples, 1979). Trace-element values for both feldspars and the bauxite are from the "supplementary information" announcement (Bureau of Analysed Samples, 1981).

The certificates for the feldspars and the sillimanite are labelled "provisional", but the 1979 catalog lists the same values for all three without qualification.

Compositions of the iron ore, slag and silica-rich samples are listed in Table 22. The apparently high summation for the iron ore may be due to the presence of ferrous iron, all of which would have been included in the "total iron, expressed as ferric oxide", thereby introducing an error in the form of oxygen which is not actually present.

Table 22. BCS iron ore, slag and high-silica materials – usable values (originators')

Per cent (dry basis)	Northamptonshire Iron ore ES-681-1	Blast Furnace Slag BCS-367	Silica Brick BCS-267	High Purity Silica BCS-313
SiO_2	17.80	34.4	95.9	99.6
TiO_2	0.48	0.75	0.17	0.022
Al_2O_3	10.62	20.0	0.85	0.16
Fe_2O_3T	47.48		†0.79	0.030
FeOT		*1.00		
MnO	0.28	1.16	†0.15	0.001?
MgO	1.48	7.1	0.06	0.005?
CaO	3.92	32.4	1.75	0.02
Na_2O	0.092	0.44	0.06	0.008?
K_2O	0.59	1.17	0.14	0.04
H_2O^+	10.4?			
CO_2	5.4?			
L.O.I.	[14.7?]			
P_2O_5	2.02	0.14?		0.14?
F	0.19			
S (total)	0.103	0.94		
SO_3 ("soluble")		[0.32]		
Others	0.24?	?		
Sum	101.09?	99.69?	99.87	100.03?
O/F,S,etc.	0.13	0.41?	?	?
Sum (corr.)	100.96?	99.28?	99.87?	100.03?
ppm				
As	100?			
C (total)	1.80(pct)			
Cr	410			
Li				3?
Ni	160			20?
Pb	70?			
V	770			

* Total iron, expressed as FeO

† Iron and manganese total contents expressed as usual oxides, but sample contains about 0.08 pct Fe and 0.10 pct Mn as free metals.

Values in square brackets not included in totals

The low total for the slag sample recalls a similar effect with CCRMP-SLg-1. With the BCS slag, the oxygen-for-sulphur correction was based on the assumption that all sulphur, other than that present as "soluble sulphur trioxide", occurred as sulphide, which might have led to an excessively large correction. However, the summation is too low regardless of the form of the sulphur in the sample. Perhaps a loss of ignition could account for the discrepancy, but the certificate makes no mention of any determination of that nature.

The values for ES-681-1 are from the catalog (Bureau of Analysed Samples, 1979). However, the catalog identifies the sample with an earlier designation as BCS-302/1. A certificate for that designation (Ridsdale, 1974) gave some data not shown in the catalog and also included some values that do not agree with those in the catalog. Because the certificate is designated as "preliminary" and the catalog was published five years later, the values from the latter were given precedence in Table 22, but additional data from the certificate were also included. The ES-681-1 designation indicates that this originally BCS sample is now recognized as a "Eurostandard".

The BCS-367 values are from Ridsdale (1970c), those for BCS-267 from Ridsdale (1955) and those for BCS-313 from Ridsdale (1965).

Finally, it must be recalled that none of the BCS samples listed in this work are actually rocks. In procedures designed for rock analysis, these materials may show anomalous behavior, as pointed out earlier. Further, the still limited information on trace-element contents not only limits the usefulness of the samples in trace-element determinations, but also hinders efforts at detecting and identifying interferences.

QMC – QUEEN MARY COLLEGE (U.K.)

(Contact: Dr. A.B. Poole, Department of Geology, Queen Mary College, University of London, Mile End Road, London E1 4NS, England).

Four proposed reference samples were prepared, apparently in relatively small quantities, in the late 1960s. According to Poole (personal communication), the samples were intended originally for internal use only but were subsequently offered to other institutions without charge. Judging from occasional reference in the literature to measurements on these samples, one may assume that they have been, or may still be, in use in an appreciable number of laboratories. At this writing, it is not known whether the samples are still available from the original source.

The originators of these samples have never published any information on them. All of our knowledge about the samples is based on what appears to be a report circulated to an unspecified audience (Poole, 1972). That report admitted that data on trace elements were limited and expressed the hope that other laboratories would report additional data for incorporation "in future reports". Unfortunately, subsequent correspondence with Poole suggested that no such future reports were to be expected.

The samples were described in the above report as follows:

I-1	Aplitic Granite from Andara Pluton, Maas, Co. Donegal.
I-3	Dolerite (Tertiary Cone Sheet) from Ardnamurchan, Inverness-shire.
M-2	Pelite (Garnet grade, Moine) from Arnipol, Arisaig, Inverness-shire.
M-3	Calc-Silicate (Garnet grade, Moine) from Morar Estuary, Inverness-shire.

The report also described the preparation of the samples and gave approximate modal analyses, but no recommended values for the chemical constituents. The values provided in Table 23 were derived by an early version of the select laboratories method, using Poole's (1972) data, to which our laboratories had not contributed. In view of the limited available data and the fact that the supply of the samples themselves may now be exhausted, no effort has been made to re-calculate values by means of later versions of the method.

The raw data for these samples include very few results for H_2O^-. Analyses which did not include that determination were therefore taken as being on the dry basis. The resulting uncertainty would affect only those constituents present at relatively high levels. Question marks have therefore been used with all usable values exceeding 10 per cent, as well as in cases where uncertainty exists for the more usual reasons.

Table 23. QMC rocks – usable values (compiler's)

Per cent (dry basis)	Aplitic Granite I-1	Dolerite I-3	Pelitic Schist M-2	Calc-Silicate M-3
SiO_2	75.36?	49.75?	48.88?	55.59?
TiO_2	0.05	2.60	0.72	0.83
Al_2O_3	13.92?	13.07?	23.97?	17.62?
Fe_2O_3	0.33?	5.09?	2.31?	0.91?
FeO	0.20?	10.04?	6.30?	3.33?
MnO	0.03	0.22	0.26	0.28
MgO	0.11	4.18	2.45	1.21
CaO	0.80	8.20	1.75	12.01?
Na_2O	4.59	2.92	1.40	2.98
K_2O	4.28	1.43	7.90	0.71
H_2O^+	0.13?	1.71?	3.21?	0.78?
CO_2	?	?	?	2.98?
P_2O_5	0.02?	0.40?	0.50?	0.36?
F	?	0.07?	0.10?	0.06?
S	0.005?	?	?	?
Others	0.10?	0.28?	0.32?	0.15?
Sum	99.93?	99.96?	100.07?	99.80?
O/F,S,etc.	0.00?	0.03?	0.04?	0.03?
Sum (corr.)	99.93?	99.93?	100.03?	99.77?
Fe_2O_3TR	0.54	16.22?	9.25	4.55
Fe_2O_3TC	0.55?	16.25?	9.31?	4.61?
ppm				
Ba	480?	690?	1550?	125?
Co		49?	30?	10?
Cr	7?	26?	56?	54?
Cu	8?	165?	130?	25?
Ga		17?	23?	17?
La		30?	120?	60?
Li		20?		
Ni		17?	36?	17?
Pb	74?	10?	17?	20?
Rb	130?	42?	310?	25?
Sc		50?	30?	
Sr	170	260	185?	500?
V	7?	500?	80?	75?
Y		50?	60?	45?
Zn	16?	100?	130?	44?
Zr	60?	190	100?	290?

ASK – ANALYTISK SPORELEMENT KOMITE

(Contact: Dr. O.H.J. Christie, Rogaland District High School, Studiesenteret Ullhandhaug, N-4001 Stavanger, Norway)

A group of laboratories in Norway, Sweden and Denmark undertook collaborative analysis of three Norwegian samples, beginning in 1968. Interest was directed mainly toward certain trace elements, but "information values" were reported for a number of major and minor constituents as well. Background information, analytical data and recommended values were reported by Andersson and Christie (1975) and by Christie (1975).

Because no attempt was made to do more comprehensive analysis, the quantity of analytical data reported was comparatively small, even for those elements for which values were eventually recommended. However, as mentioned earlier, those values resulted from face-to-face discussions between collaborating analysts. It may therefore be concluded that their decisions were based on knowledgeable understanding of both the nature of the samples and of the strengths and weaknesses of the various analytical approaches.

The three samples were described as follows:

ASK-1:	Larvikite from Tvedalen quarry, southwest of Larvik, Vestfold county, south Norway, a type locality of the light-coloured variety of Larvikite.
ASK-2:	Schist from the Upper Tremadoc Ceratopyge schist [3b of the Oslo region Arenigan (Lower Ordovician)] in the underground of St. Olavs pass.
ASK-3:	Sulphide ore containing over 40 per cent sulphur and therefore not included in this compilation because its composition is far removed from that of silicate rocks.

Table 24 lists the "uncertified concentration values"and "recommended trace concentration values" (Christie, 1975). The former are listed in parentheses, the latter without qualification. Some of the trace-element values have been rounded, to facilitate comparison with data on other samples in this compilation.

Table 24. ASK rocks – usable (and information) values (originators')

Per cent (dry basis)	Larvikite ASK-1	Schist ASK-2
SiO_2	*(59.5)	(54.2)
TiO_2	(1.1)	(0.92)
Al_2O_3	(18.6)	(18.8)
Fe_2O_3T	(4.6)	(6.9)
MnO	0.132	0.036
MgO	(1.1)	(2.0)
CaO	(3.2)	(0.75)
Na_2O	(6.5)	(0.8)
K_2O	(4.2)	(5.3)
C (total)		(8.5)
ppm		
Ag	0.05	0.4
B		155
Ba	1150	
Be	4	4
Cl	100	14
Co	6	27
Cr	40	90
Cs	1.5	11
Cu	7	120
Ga	29	25
Li	18	30
Mo		60
Ni	110	150
Rb	85	175
Sc	7	
Sr	680	100
V	49	220
Zn	105	165
Zr	400	170

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*Analyses are not complete
Bracketed figures are not usable values

IRSID – INSTITUT DE RECHERCHES DE LA SIDÉRURGIE (France)

(Contact: G. Jecko, Institut de Recherches de la Sidérurgie, Station d'essais, 57210 Maizières-lès-Metz, France)

This institute has produced many reference samples of value to the ferrous metallurgical industry. Only two of those have been selected for inclusion in this compilation because their compositions may prove useful in the analysis of silicate rocks and minerals.

Our own laboratories were not involved in any IRSID evaluations.

One of the samples is a blast furnace slag, ES-878-1, a Eurostandard formerly listed as LO1-1. The values listed in Table 25 are recalculated as oxides from Jecko (undated). The other sample, a ferriferous marl, is designated MO8-1. Its values in Table 25 are recalculated from Jecko (1970). In both cases, the values listed without question marks are based on those listed as "most probable" on the certificates. Those with question marks include some shown on the certificates "representing only indications" (author's translation) and some reported by the originators in a private communication. Some of the values have been rounded for this compilation.

Table 25. IRSID samples – usable values (originators')

Per cent (dry basis)	Blast Furnace Slag ES-878-1	Ferriferous Marl MO8-1
SiO_2	33.65	60.39
TiO_2	0.62	0.71
Al_2O_3	16.15	9.94
Fe_2O_3		3.08
FeO		2.38
Fe_2O_3T	0.86	†[5.72]
MnO	1.27	0.06
MgO	9.55	1.34
CaO	35.65	8.70
Na_2O	0.47	0.5?
K_2O	1.29	2.2?
H_2O^+		3.0?
CO_2		*7.3
P_2O_5	0.034?	0.12
F	0.15	0.014
S	0.81	0.46?
Others	?	0.05?
Sum	100.50?	100.25?
O/F,S,etc.	0.47	0.24?
Sum (corr.)	100.03?	100.01
ppm		
As		30?
Cr		130?
Cu		35?
Ni		50?
Pb		35?
V		130?
Zn		50?

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* Total C, expressed as CO_2
† Not counted in summation

CRPG – CENTRE DE RECHERCHES PÉTROGRAPHIQUES ET GÉOCHIMIQUES
ANRT – ASSOCIATION NATIONALE DE LA RECHERCHE TECHNIQUE
GIT-IWG–GROUPE INTERNAITONAL DE TRAVAIL/ INTERNATIONAL WORKING GROUP

(Contact: K. Govindaraju, Centre de Recherches Pétrographiques et Géochimiques, B.P. No 20, 54501 Vandoeuvre-Nancy Cedex, France).

This group rivals, and in some aspects surpasses the achievements of the U.S. Geological Survey in terms of the production and evaluation of reference materials of silicate rocks and minerals. CRPG-ANRT-GIT-IWG may not have produced as many samples, but they have certainly done a more thorough and systematic job in the compilation of results and derivation of usable values. Much of the credit for such work belongs to one individual – K. Govindaraju.

All of the preparation and co-ordination of the work on these reference samples has been done at CRPG, and the earlier materials were identified with that institute. Later work was done as a function of ANRT and samples accordingly designated as products of that association, even though CRPG was involved to the same extent as it was with the samples that bore its own name. Still later, the reference samples originating at or processed by CRPG became identified with GIT-IWG, the group associated with the Geostandards Newsletter.

Table 26. CRPG rocks – usable values (originators')

Per cent (dry basis)	Granite GR	Granite GA	Granite GH	Basalt BR
SiO_2	65.97	69.96	75.85	38.39
TiO_2	0.65	0.38	0.08	2.61
Al_2O_3	14.76	14.51	12.51	10.25
Fe_2O_3	1.65	1.36	0.41	5.61
FeO	2.16	1.32	0.84	6.60
MnO	0.06	0.09	0.05	0.20
MgO	2.40	0.95	0.03	13.35
CaO	2.50	2.45	0.69	13.87
Na_2O	3.80	3.55	3.85	3.07
K_2O	4.50	4.03	4.76	1.41
H_2O^+	0.70	0.87	0.46	2.31
CO_2	0.26	0.11	0.14	0.86
P_2O_5	0.28	0.12	0.01	1.05
F	0.10	0.05	0.35	0.10
S	0.01?	0.02?	?	0.04?
Others	0.33?	0.25?	0.13?	0.56?
Sum	100.13?	100.02?	100.17?	100.28?
O/F,S,Cl	0.05?	0.04?	0.15?	0.07?
Sum (corr.)	100.08?	99.98?	100.02?	100.21?
Fe_2O_3TR	4.04	2.77	1.36	12.90
Fe_2O_3TC	4.05	2.83	1.34	12.94
ppm				
B	6?	20		10?
Ba	1050	850	22	1050
Be	5.5	3.6	6?	1?
Ce		70	50?	140
Cl		300?	100?	370?
Co	10	5	1.5?	50
Cr	110	12	6	380
Cs		6	2.5	1.3?
Cu	340	16	14	72
Dy			7?	
Eu				3.7?
Ga	20	16	23	20
La	75?	38	25?	80
Li	55?	90	45?	13
Mo	18?	1	3?	3?
Nb		10?	85?	100?
Nd		25?	25?	60?
Ni	55	7	3	260
Pb	32	30	45	8
Rb	175	175	390	47
Sc	7?	7	1?	26?
Sm		5?	10?	12?
Sn	10?	4?	10?	8?
Sr	550	310	10	1300
Th		17	90?	12?
U		4?	18?	3?
V	65	38	5?	240
Y	19?	21	70	30
Yb	2	2?	8?	2?
Zn	60	80	85	150
Zr	180	150	150	250

For purposes of the compilation, the CRPG-ANRT-GIT-IWG samples have been divided into six groups: CRPG rocks, CRPG micas, two "generations" of ANRT samples and two groups of GIT-IWG samples. These are described in the sections that follow.

CRPG rocks

The earliest work on reference materials at CRPG was done on an "experimental granite", GR, described by Roubault et al. (1964) merely as calco-alkaline granite from Senones (Vosges). It was prepared in relatively small quantity and its supply was exhausted in a short time. For that reason, it was not included in earlier compilations in this series (Abbey, 1972, 1973b, 1975b, 1977b, 1980). However, because limited amounts of the material may still be present in some laboratories, it was decided to include it in this work.

Shortly after the experimental work on GR was done, three additional samples were prepared: BR, a basalt from Essey la Côte, in Lorraine; GA, another calco-alkaline granite, but this time from Andlau (Vosges); and GH, described merely as "acid granite (Hoggar)".

Analytical data compilations, including GSC contributions, and derived "recommended" or "proposed" values were published in a series of reports (Roubault et al., 1966, 1968, 1970; Govindaraju and de la Roche, 1977). In the first three reports, the mean of values remaining after elimination of all that differed from the overall mean for each major or minor constituent by more than one standard deviation was taken as "recommended value". However, if the dispersal of reported results appeared excessive, or too few in number, only an approximate "proposed value" was assigned. Such values are shown in Table 26 and the other tables on the CRPG-ANRT-GIT-IWG samples with question marks.

For trace elements, recommended or proposed values were based on a subjective scanning of all available results. In the most recent report on the CRPG rocks (Govindaraju and de la Roche, 1977), which covered only trace elements, the available results were examined more closely, and broken into subgroups on the basis of methods used. A good background knowledge of the limitations of methods can be very useful in aiding subjective judgment in assigning a "best value". On the other hand, the "methods" considered were, in general, merely techniques of final measurement (atomic absorption, colorimetry, x-ray fluorescence, photographic emission spectroscopy, photoelectric emission spectroscopy, etc.), with little concern for mode of sample attack and other pre-treatments. Thus the degree of dispersion of results by a particular technique may depend more on differences in pre-treatment than on the inherent reliability of the technique. However, the assigned values for the CRPG rocks appear to be of high quality, according to experience in GSC laboratories. As shown in Table 26, major and minor constituents (including trace elements on GR only) are based on Roubault et al. (1970); those on trace elements in the other samples on Govindaraju and de la Roche (1977). Some of the higher trace-element values have been rounded to conform with other data in this work.

At this writing, supplies of BR are believed to be exhausted. However, replacements for both GR and BR are included among the samples described in the following sections.

CRPG micas

Two micas were prepared for use as reference materials. The biotite, Mica Fe, was reported by Roubault et al. (1968) as coming from "Piles of biotite in the Massif of Point-Sylvestre (Massif Central, France)" and collected "Near the National Road 20, north of Limoges...". The same reference described the phlogopite, Mica Mg, as coming from phlogopite deposits of Bekily, in southern Madagascar. These samples were prepared in smaller quantities than were the CRPG rocks – as might be expected from the nature of the samples. Nevertheless, their compositions have proved useful in calibrations because the concentrations of some constituents in both samples have served to extend working ranges.

A great deal more analytical data have always been available for Mica Fe than for Mica Mg; for that reason, the most recent compilation (Govindaraju, 1979), which included major contributions from our laboratories, listed only "proposed" values for the latter sample. However, examination of the tables in that reference indicates that, for some constituents at least, the dispersion of results for Mica Mg were no worse than for Mica Fe, even though the number of results was always smaller for the former. In this work, it was decided to consider such values as the equivalent of recommended values, provided they were based on at least 10 reported results.

The values listed in Table 27 are based entirely on those of Govindaraju (1979), except that some have been "upgraded" as stated in the preceding paragraph, all major and minor constituents have been converted to the dry basis and values for several trace elements have been rounded.

In evaluating the data on these two samples, Govindaraju (1979) made a radical departure from earlier practice. For each major and minor constituent, a number of statistical parameters were computed: the arithmetic mean, standard deviation, skewness, "preferred mean" (mean after eliminating results beyond one standard deviation of the overall mean), gamma central value and dominant cluster mode. Further, those parameters were determined not only for all available results but also for results classified by analytical method. The breakdown was based in some cases on a separation of "chemical" from "physical" methods, in others on a "fine-structure" resolution among the physical methods. Choice of assigned value was based on knowledgeably subjective decisions after examining all available data.

Advantages and disadvantages of a similar approach have been mentioned above in connection with the CRPG rocks. In this case, the matter is further complicated by uncertainty of what constitutes a "physical" or "chemical" method. Thus if a sample is dissolved by acid treatment or fusion and an analyte measured by means of atomic absorption or with an ion-selective electrode, is the method chemical or physical? There are significant chemical and physical aspects to nearly all analytical methods, whether they are considered "wet" or "instrumental". In some cases, it is merely a matter of degree, and it is therefore difficult to draw a distinct boundary between the two.

For the samples in Table 27 (and for all but one of the ANRT samples that follow), the originators did not derive a ferric iron value from results reported as such, but merely calculated ferric iron by difference from the derived values for total iron and ferrous. Where such a procedure was followed, the iron-oxide compatibility test becomes meaningless; no value for Fe_2O_3TC is therefore shown in such cases.

ANRT I

The first four reference materials produced under the ANRT label were a diorite DR-N; a serpentine UB-N, a bauxite BX-N and a kyanite ("disthène" in French) DT-N. DR-N was described by de la Roche and Govindaraju (1969) as "a silicate rock selected in the range of 'mean compositions of the lithosphere' estimated by various

Table 27. CRPG micas – usable values (originator's – slightly modified – see text)

Per cent (dry basis)	Biotite Mica-Fe	Phlogopite Mica-Mg
SiO_2	34.55	38.42
TiO_2	2.51	1.64
Al_2O_3	19.58	15.25
Fe_2O_3	4.66	1.99?
FeO	18.99	6.75?
MnO	0.35	0.26
MgO	4.57	20.46
CaO	0.43	0.08?
Na_2O	0.30	0.12?
K_2O	8.79	10.03
H_2O^+	2.92?	2.10?
CO_2	0.19?	0.15?
P_2O_5	0.45	0.01?
F	1.58	2.85?
S	0.01?	0.02?
Others	1.09?	0.80?
Sum	100.97?	100.93?
O/F,S,Cl	0.68?	1.23?
Sum (corr.)	100.29?	99.70?
Fe_2O_3TR	25.76	9.49?
ppm		
Ba	145	4000
Be	8?	
Ce	370?	
Cl	500?	800?
Co	20	20?
Cr	90	100
Cs	200?	55?
Cu	4?	4?
Ga	95	21?
Hf	17?	
Li	1400	120?
La	190?	
Nb	270?	120?
Ni	35	110
Pb	13?	9?
Rb	2200	1300
Sn	70?	
Sr	5	25
Ta	34?	
Th	150?	
U	60?	0.5?
V	135?	90?
Y	25?	
Zn	1300	290
Zr	800?	20?

authors" (author's translation). UB-N is described in the same reference merely as "an ultrabasic rock SERPENTINE". Later, de la Roche and Govindaraju (1971) described BX-N merely as "an aluminum ore Bauxite", and DT-N as "a Silico-aluminous refractory mineral Disthène (Kyanite)". Analytical data and some derived values were reported by those authors in both of the foregoing references. A more extensive compilation appeared a few years later (de la Roche and Govindaraju, 1973a). The most recent information on these samples was reported by Govindaraju (1982); the values from that source are given in Table 28, the only difference being that they have been converted to the dry basis, using Govindaraju's recommended values for H_2O^- for each sample.

The GSC Analytical Chemistry Section was one of the major contributors of analytical data used in the evaluation of these samples. Govindaraju's method for arriving at the derived values is described in the section on GIT-IWG.

ANRT II

The second group of four ANRT materials is of even more varied nature than the samples here designated as ANRT I. It includes a granite, a feldspar, a glauconite and a synthetic glass.

GS-N was described by de la Roche and Govindaraju (1976) as a calco-alkaline granite, collected on road D49 between Senones and Launois, and probably intended as a replacement for the exhausted GR. The same reference mentions FK-N as a potash feldspar, obtained through an importer from the general area of Madras, India, exact location unknown.

In assigning concentration values for major and minor constituents to GS-N and FK-N, de la Roche and Govindaraju (1976) computed means, medians, standard deviations, "preferred means" and "preferred medians", both for all results and for results based on particular analytical techniques, then arrived at recommended or proposed values by subjective considerations. For trace elements, the choice was almost entirely subjective, generally involving the median of available results. All assigned values for trace elements in GS-N and FK-N are therefore "proposed", not "recommended". For purposes of this compilation, the distribution of individual results for trace elements have been compared to distributions in earlier CRPG and ANRT samples where recommended values had been assigned. As a result, some trace elements in GS-N and FK-N are shown in Table 29 without question marks. GSC laboratories contributed some data to this evaluation.

The assigned values for ferric iron for the two samples were determined by difference between the assigned values for total iron and ferrous. No Fe_2O_3TC is therefore shown for either sample in Table 29.

GL-O, the glauconite, was produced for use as a reference material in geochronology (Odin et al., 1976). It was separated from "...fresh rock collected on a cliff... [overlooking]... the beach at Cauville (Basse-Normandie, 20 km north of Le Havre)" (author's translation). Later, de la Roche et al. (1976) described detailed collaborative analytical work on the sample, deriving usable values in much the same manner as done with GS-N and FK-N. The sample thus qualifies for use as reference material in general rock analysis, although the available quantity is limited.

The fourth sample in this arbitrary group is something very different from all other CRPG-ANRT-GIT-IWG materials. VS-N is a synthetic glass of "phonolitic" composition (de la Roche and Govindaraju, 1973b) in which 28 "trace" elements have been added to the silicate matrix. The target concentrations for most of the additives were 1000 ppm of the appropriate oxide, 500 ppm for two oxides (gallium and scandium). Several batches of preliminary material were prepared and analyzed before the final material was produced and subjected to collaborative analysis, which revealed that the concentrations of most of the additives were close to their target values. In Table 29, the values listed for most of the major and minor constituents are based on the originator's "preferred means", but are for information only; they are not usable values.

Table 28. ANRT I – usable values (originators')

Per cent (dry basis)	Diorite DR-N	Serpentine UB-N	Bauxite BX-N	Kyanite DT-N
SiO_2	52.98	39.93	7.43	36.50
TiO_2	1.09	0.11	2.38	1.40
Al_2O_3	17.56	2.94	54.45	59.29
Fe_2O_3	3.71	5.43	22.98	0.55
FeO	5.41	2.71	0.26	0.10
MnO	0.22	0.12	0.05	0.008
MgO	4.41	35.66	0.11	0.04
CaO	7.07	1.22	0.17	0.04
Na_2O	3.00	0.10	0.04	0.04
K_2O	1.70	0.02	0.05	0.12
H_2O^+	2.26	10.98	11.53	0.90
CO_2	0.10	0.39	0.44	?
P_2O_5	0.25	0.04	0.13	0.09
F	0.047?	?	?	?
S	?	?	?	?
Others	0.25?	0.76?	0.39?	0.77?
Sum	100.05?	100.41?	100.41?	99.85?
O/F, S, Cl	0.03?	0.02?	0.00?	0.00?
Sum (corr.)	100.02?	100.39?	100.41?	99.85?
Fe_2O_3TR	9.72	8.45	23.27	0.66
ppm				
As	3?	12?	120?	
B		145?		
Ba	390	30?	34?	130?
Be	1.8?		5.5?	
C (non-$CO_3^=$)				6200
Cd	0.09?			
Ce	46		500?	125?
Cl	400?	800?		
Co	35	110	35?	12?
Cr	42	2300	300?	240?
Cs	6	11?		
Cu	50	28	18?	9?
Eu	1.5?		3.9?	1.5?
Ga	22?	5?	70?	30?
Gd	3.5?			
Hf	2.7?			9?
La	21?		390?	
Li	42	28?		
Nb	6?			
Nd	22?			48?
Ni	16	2000	200?	16?
Pb	55	18	135?	28?
Rb	70	6?		
Sb	0.3?	0.26?		0.2?
Sc	28?	13.5?	60?	2.3?
Sm	5.3?			
Sr	400	10	110?	27?
Ta	0.7?		4?	2.7?
Tb	0.8?			
Th	5		55?	13.5?
U	1.5		8?	2.3?
V	230	75	310?	160?
Y	30?	11?	120?	
Yb	2.8?			
Zn	145	92?	60?	28?
Zr	125	8?	520?	370?

Table 29. ANRT II – usable (and information) values (originators')

Per cent (dry basis)	Granite GS-N	Potash Feldspar FK-N	Glauconite *GL-O	Synthetic Glass VS-N
SiO_2	65.98	65.11	52.22	*(56)
TiO_2	0.68	0.02?	0.07?	(1.1)
Al_2O_3	14.71	18.64	7.75	(13.5)
Fe_2O_3	1.93	0.024?	17.61	
FeO	1.65	0.06?	2.25	
Fe_2O_3T	*[3.76]	*[0.09?]	*[20.11]	(4.1)
MnO	0.056	0.005?	0.008?	0.11
MgO	2.31	0.01?	4.58	(4.5)
CaO	2.51	0.11	0.98	(4.6)
Na_2O	3.78	2.58	0.04?	(6.0)
K_2O	4.64	12.83	8.16	(8.1)
H_2O^+	1.07	0.32?	5.72	
CO_2	0.18?	0.085?	?	
P_2O_5	0.28	0.024?	0.38	
F	0.01?	0.00?	0.15?	
S	0.01?	0.00?	?	
Others	0.33?	0.14?	0.07?	
Sum	100.12?	99.96?	99.98?	
O/F,S,Cl	0.01?	0.00?	0.06?	
Sum (corr.)	100.11?	99.96?	99.93?	Incomplete
ppm				
B				300?
Ba	1400	210?		1000
Bi				1000?
Cd				900?
Ce				(800)
Co	65	16?	17?	700
Cr	55	3?	140?	700
Cs		7?		900?
Cu	20	3?	5?	800
Ga				400
Li	55?		70?	(500)
Mo				700?
Nb				(700)
Ni	34	3?	36?	800
Pb	60	240		1000
Rb	190?	850?	240	800?
Sb				800?
Sc				300?
Sn				800?
Sr	570	35?	19	700?
Ta				(900)
V	62?			600?
Y		13?		(800)
Yb				900?
Zn	48	24?	43?	800
Zr	240?			700?

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* Notes

Values in parentheses are magnitudes only, not usable values
Values in square brackets are not included in totals
GL-O values based on sample dried 15 hr. at 105°C

The originators' recommended and proposed values for oxides of "trace elements" were rounded by them to approximately the nearest 100 ppm. Those listed in Table 29 are similarly rounded versions of the elemental equivalents of the originators' unrounded preferred means of oxides in the case of their recommended values, and of their rounded proposed values.

A synthetic material like VS-N can be considered as potentially useful because of its known contents of so many trace elements. The objection that the additives are present in quantities much higher than most of them occur in natural rocks can possibly be overcome by preparing dilutions of VS-N with "pure" base material. However, such a procedure has two disadvantages:

(a) The base material may not be as pure as desirable, or contamination can occur in the dilution process. (VS-N was found to have been contaminated with measurable amounts of Ag, As, Br, Cl, FeO, In, P, S and Se in processing.)

(b) Repeated dilution of VS-N would not materially change the relative concentration ratios of the various additives. Analytical interferences would therefore be more difficult to detect.

For the above reasons, some analysts have questioned the value of synthetic reference materials similar to VS-N. Others may find it useful. From the point of view of this work, the most interesting aspect of the work done on VS-N lies in the dispersion of data reported for each constituent. Because VS-N is a glass, one might expect that it would be much more homogeneous than a multi-phase sample like a rock. Yet the distribution of results – for major, minor and trace constituents – appears to be no more coherent than is usually the case with rock samples, thus adding another point to the argument that interlaboratory factors are much more important than possible sample inhomogeneity. (Our laboratories have not been involved in the evaluation of VS-N.)

Finally, in view of the highly varied nature of the samples in group ANRT II, the reader's attention is directed to the notes at the bottom of Table 29.

GIT-IWG

This group consists of three samples, described as follows (Govindaraju, 1980):

AN-G: an anorthosite from the Fiskenaesset stratified basic complex in the northern part of Qeqertarssuatsiaq island, Greenland.

BE-N: a basalt from Essey-la-Côte, Meurthe-et-Moselle, France, essentially from the same source as the now exhausted BR, and intended as a replacement for that sample.

MA-N: an albite-lepidolite granite from north of Clermont-Ferrand, France

The above superficial notes on the nature of these samples reveals nothing about the veritable tour-de-force achieved by the originators of the materials. In the short space of less than a year, portions of the three samples were distributed to over 100 laboratories all over the world (including the GSC Analytical Chemistry Section), analyses performed, results reported, the data collated and interpreted, assigned values arrived at and a 90-page report published (Govindaraju, 1980). In that paper Govindaraju went to great pains to express his gratitude to the 243 analysts in 122 laboratories, located in 25 different countries, for the over 6000 results they reported. He mentioned little, as might be expected, about the prodigious task he undertook, starting with those 6000 results, not to mention the staggering logistics of initially processing about a ton of each sample material.

Table 30. GIT-IWG rocks – usable values (originators', slightly modified – See text)

Per cent (dry basis)	Anorthosite AN-G	Basalt BE-N	Granite MA-N
SiO_2	46.35	38.39	66.74
TiO_2	0.22	2.62	0.01
Al_2O_3	29.83	10.12	17.66
Fe_2O_3	0.87	5.37	0.13
FeO	2.24	6.77	0.31
MnO	0.04	0.20	0.04
MgO	1.80	13.22	0.04
CaO	15.92	13.94	0.59
Na_2O	1.63	3.20	5.85
K_2O	0.13	1.40	3.19
H_2O^+	0.61	2.25	1.08
CO_2	0.13	0.74	0.13
P_2O_5	0.01	1.06	1.39
F	0.012?	0.10?	1.70
S	0.014?	0.03?	0.01?
Others	0.07?	0.56?	1.87?
Sum	99.88?	99.97?	100.74?
O/F,S,Cl	0.02?	0.06?	0.72?
Sum (corr.)	99.86?	99.91?	100.02?
Fe_2O_3TR	3.36	12.90	0.47
ppm			
Ag			2
As			13?
B			17?
Ba	34	1050	42
Be			280
Cd			2?
Ce	4.7	150	10?
Cl	300?	300?	140?
Co	25	61	1?
Cr	50	360	3?
Cs		0.8?	640
Cu	19	72	140
Eu	0.37?	3.6?	
Ga	18	17	59
Gd		9?	
Hf	0.38?	5.4?	4.5?
La	2	82	1?
Li	13	12	4900
Lu	0.12?	0.24?	
Nb	2?	100	175
Nd	2?	70	
Ni	35	270	3?
Pb	2?	4?	29
Rb	1?	47	3600
Sb			1.9?
Sc	10	22	0.24?
Sm	0.7?	12	
Sn			1050?
Sr	76	1350	84
Ta	0.2?	5.5?	310?
Tb	0.2?	1.3?	
Th		11	1?
U		2.4	12?
V	70	240	4.6?
W	90?	29?	70?
Y	8	30	1?
Yb	0.85	1.8	
Zn	20	120	220
Zr	15	270	27?

In the course of the data processing, for each constituent of each sample, where there were sufficient data to justify such action, the median, mean, standard deviation, skewness, preferred mean, gamma central value, dominant cluster mode and geometric mean were computed, as well as a "preferred mean of five central values" (median, preferred mean, gamma central value, dominant cluster mode, geometric mean). To quote Govindaraju (1980): "These five evaluators... were calculated... also on specific sets of data obtained by individual or assimilated methods of analysis...". Assigned values were then deduced by subjective choice among the many computed "central values".

Govindaraju extended his modesty even to the derived values in designating all as merely "proposed values", expressing the intention "...to study more in detail the data.... for promoting the proposed values to a higher grade of recommended values". In fact, it appears that both the quantities of raw data and the interpretive work to which they had been subjected were much greater in this case then in all CRPG-ANRT sets of samples, in many of which recommended values were assigned. One may well ask what more one can wish to have to establish good assigned values.

Accordingly, many of the values shown in Table 30 are shown without question marks. The decision to do so or not was made in most cases on the basis of the number of results reported, in other cases on the relative coherence of those results. Some trace-element values have also been rounded.

We know that Govindaraju derived values for Fe_2O_3 in these samples by difference from the respective derived values for Fe_2O_3T and FeO. As pointed out earlier, such action renders the iron-oxide compatibility test meaningless. The question now arises: What would the iron-oxide compatibility test have shown if Govindaraju had actually derived values directly from reported results for Fe_2O_3?

Table 31 lists the five "central values" (Govindaraju, 1980) and their preferred means for Fe_2O_3 in the three samples, all converted to the dry basis. Using the Fe_2O_3 equivalents of Govindaraju's proposed values for FeO, values for Fe_2O_3TC were computed for each of the central values and for the preferred mean of central values, and compared to Govindaraju's proposed values for Fe_2O_3TR.

As shown in Table 31, the median would have given the best compatibility for AN-G, the dominant cluster mode for the other two samples. Unfortunately, the dominant cluster mode gave the worst compatibility for AN-G. Had the central value with the best iron-oxide compatibility been taken as the assigned value for each sample, the three Fe_2O_3 values would have become 0.88, 5.39 and 0.14, all slightly higher than Govindaraju's 0.87, 5.37 and 0.13, with corresponding slight increases in the summations. Had the preferred means of central values been favoured, the Fe_2O_3 values would have become 0.90, 5.42 and 0.16, a somewhat larger increase over Govindaraju's proposed values, with summations of 99.89, 99.96 and 100.05.

Although all of the above possible changes are small and all of the possible iron-oxide compatibilities well within the range of acceptibility, they do point to two phenomena that are worth further study: (a) the expected slight positive bias in Fe_2O_3 determinations (corresponding to the negative bias in FeO results), and/or (b) the validity of the use of the five central values or their preferred mean as indicators of best value.

In any event, these three samples will likely prove useful to geoanalysts, particularly MA-N, because of its unusually high contents of Be, Cs, Ga, Li, Nb, Rb, Sn, Ta and W.

Other GIT-IWG materials

Preparation of an iron formation rock reference sample, designated IF-G, is under way at CRPG (Govindaraju, personal communication). The material was collected in the field by the Geological Survey of Greenland, following a proposal by Uitterdijk Appel (1980). At this writing, no analytical work on the sample has been published. An albite sample, AL-I, is also in preparation (de la Roche and Govindaraju, 1982).

Plans for the preparation of a series of synthetic "glass calibration standards" were announced by de la Roche and Govindaraju (1975). The intention was to prepare synthetic glasses with compositions close to those of existing rock reference samples, as well as one containing somewhat less of each constituent and another somewhat more, than contained in the "target composition" corresponding to each existing rock sample. As far as is known at this writing, no further information has appeared in the literature.

In view of the excellent work of CRPG, ANRT and GIT-IWG in reference rocks in the past, one may expect many more interesting and useful developments in the future.

Table 31. A comparison of values for iron oxides in three GIT-IWG rocks (all values in per cent, dry basis)

		AN-G	BE-N	MA-N
Fe_2O_3	Median (a)	0.88	5.42	0.17
	Preferred mean (b)	0.90	5.41	0.18
	Gamma central value (c)	0.90	5.50	0.17
	Dominant cluster mode (d)	0.82	5.39	0.14
	Geometric mean (e)	0.91	5.47	0.15
	Preferred mean of central values (f)	0.90	5.42	0.16
FeO	Proposed value (Govindaraju, 1980)	2.24	6.77	0.31
	Fe_2O_3 equivalent of FeO (g)	2.49	7.52	0.34
Fe_2O_3TR	Proposed value (Govindaraju, 1980)	3.36	12.90	0.47
Fe_2O_3TC	(a + g)	3.37	12.94	0.51
	(b + g)	3.39	12.93	0.52
	(c + g)	3.39	13.02	0.51
	(d + g)	3.31	12.91	0.48
	(e + g)	3.40	12.99	0.49
	(f + g)	3.39	12.94	0.50

IAEA – INTERNATIONAL ATOMIC ENERGY AGENCY

(Contact: IAEA, Analytical Quality Control Services, Laboratory Seibersdorf, P.O. Box 100, A-1400 Vienna, Austria)

This agency has produced a number of reference materials, generally of special interest in nuclear applications. Only two of them, a soil and a lake sediment, appear to be useful in rock analysis. Our laboratories were not involved in the evaluation of either sample.

The soil sample, SOIL-5, was described by Dybczynski et al. (1979). It was collected at the Agriculture Experimental Station La Molina, Lima, Peru (20 cm topsoil depth) (IAEA, 1978). The sediment sample was designated SL-1, but as pointed out earlier, that designation had already been used to identify a CCRMP slag, so the IAEA lake sediment is referred to as SdL-1 in this paper. It was collected by scientists of the U.S. Department of Agriculture at the Sardis Reservoir, Panola County, Mississippi, U.S.A., at a water depth of 15 m (IAEA, 1979).

The values listed for these two samples in Table 32 were derived as described earlier in this paper (Dybczynski, 1980). Briefly the procedure involves computation of means, after using several statistical tests to eliminate outliers. The listed values are categorized by the originators as (a) those recommended "with a relatively high degree of confidence", (b) those recommended "with a reasonable degree of confidence" and (c) those given for information only. In this paper, values listed by the originators under (c) are shown with question marks; those in the other two categories are shown as unquestioned usable values. Some have been rounded.

Some comment on the evaluation procedure used for these samples may be found earlier in this paper, under "Means". Although Dybczynski et al. (1979) indicated in their compilation of data on SOIL-5 that some of the results involved pre-treatment of the sample, or even separations, they did not specify the actual treatment in each case. They then proceeded to a "comparison of the methods", a comparison really between the results obtained by the various techniques of final measurement. Possible sources of error in the pre-treatments (e.g. incomplete recoveries) were therefore overlooked and the effect of such errors would then fall undeservedly on the measurement technique. For example, such techniques as atomic absorption generally require dissolution of the sample, but some analysts may not use as complete a treatment as do others, with a resulting polymodal distribution of data. In other words, a highly dispersed distribution of atomic-absorption results may be erroneously regarded as evidence of poor precision in measurement; in fact, it may be the result of inconsistencies in sample decomposition techniques.

Further information on other reference materials available from IAEA may be obtained from their offices (IAEA, 1982).

The summation of SOIL-5 in Table 32 is excessively high; none was calculated for SdL-1 because of the absence of a value for silica. The discrepancy in the former case may be the result of the arbitrary assumption that the major and minor constituents occur in the form of the listed oxides. It is difficult to postulate other forms in which they may actually occur, particularly if such forms are expected to reduce the magnitude of the sum. Also, it is noteworthy that no values have been assigned for water, carbon (in any form) or loss on ignition. Another possible source of error may lie in the manner in which the assigned values were established. In the section of this report labelled "Means", there was mention of the possibility that a derivation scheme that worked very well, on the data from a collaborative analysis of a homogeneous aqueous solution, might run into difficulties on application to a comparatively heterogeneous solid material, such as a rock or soil.

Table 32. IAEA soil and sediment – usable values (originators')

Per cent *(dry basis)	SOIL-5	Lake Sediment SdL-1
SiO_2	71 ?	
TiO_2	0.78	0.86
Al_2O_3	15.47	†(16.8)
Fe_2O_3T	6.36	9.64
MnO	0.11	0.44
MgO	2.5?	4.8?
CaO	3.1?	0.35?
Na_2O	2.59	0.23
K_2O	2.24	1.8?
H_2O^+	?	
CO_2	?	
P_2O_5	0.25?	(0.19)
F	(0.06)	
S		1.2?
Others	0.40?	
Sum	104.86?	Incomplete
(O/F,S,etc.)	0.03?	
Sum (corr.)	104.83?	
ppm		
Ag	2?	(0.08)
As	94	28
Au		0.01?
B	†(63)	(39)
Ba	560	640
Be	2?	
Bi	12?	(1)
Br	5	7
Cd	1.5?	0.26
Ce	60	115
Cl		(10)
Co	15	20
Cr	29	105
Cs	57	7
Cu	77	30
Dy	4	7
Eu	1.2	1.6?
Ga	18	24?
Gd	35?	(12)
Ge	(2)	25?
Hf	6.3	4.2
Hg	0.8?	0.1?
Ho	0.8?	(1.3)
I	(35)	(28)
In		(0.2)
Ir		(0.008)
La	28	53
Li	52?	29?
Lu	0.34	0.5?
Mo	2?	1.3?
Nb	9?	(17)
Nd	30	44
Ni	13?	45
Pb	130	38
Pr	5?	
Pt		(0.4)

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* Dried 24 hr. at 105°C

† (Values in parentheses are magnitudes only, not usable values)

Table 32 (cont.)

ppm	SOIL-5	Lake Sediment SdL-1
Rb	140	115
Ru		(0.1)
Sb	14	1.3
Sc	15	17
Se	1?	3?
Sm	5.4	9
Sn	(4)	(4)
Sr	330?	80?
Ta	0.76	1.6?
Tb	0.66	1.4?
Te		(2)
Th	11	14
Tm	0.4?	(0.7)
U	3.2	4.0
V	150?	170
W	5?	6?
Y	21?	85?
Yb	2.2	3
Zn	370	220
Zr	220?	240?

IGB – INSTITUTE OF GEOLOGY, BULGARIA

(Contact: Prof. El. Al. Ivanov, Institute of Geology, Bulgarian Academy of Sciences, Sofia, Bulgaria).

Although it has been common knowledge for some years that a Bulgarian granite reference sample was being prepared, the only published reference, to this author's knowledge, is that of Ivanov (1981), who described the sample, G-B, as a granite from the "'Granitovski' massif of the Laramide hypabyssal series in the Sredna Gora region" (author's translation from the French).

Seven Eastern European laboratories have analyzed the sample for major and minor constituents, producing results in reasonable agreement with one another. Ivanov reported trace-element results from his own laboratory only, although a few elements were determined by several different methods.

In order to arrive at the values listed in Table 33, all of the results for major and minor constituents were first converted to the dry basis, using H_2O^- values reported by each laboratory to adjust its other results. The median of all available results was then taken as a first approximation of usable value. (In the case of manganese and titanium, the values listed by Ivanov under "trace elements" were included in determining the median value of each of those elements as minor-constituent oxides). Considerable subjective judgment was involved in the case of the trace elements.

Because of the limited data available, nearly all values in Table 33 are shown with question marks or in parentheses. MnO is the exception; five of the nine reported results were 0.11 per cent, another was 0.10. The usable value of 0.11 per cent MnO is therefore shown as firmly established.

In calculating the "Others" for Table 33, several elements were included without their being listed with usable values. The reason was that only one result was available for each constituent, and all came from the originating laboratory. None were therefore considered adequate as usable values, but most were regarded as sufficiently reliable approximations such that their sum would not be in error by more than about 0.01 per cent. The comparatively good summation and iron-oxide compatibility for this sample are encouraging, but there are too few results to justify more certain usable values.

Table 33. IGB granite – usable values (compiler's)

Per cent (dry basis)	Granite G-B
SiO_2	66.89?
TiO_2	0.35?
Al_2O_3	16.25?
Fe_2O_3	1.70?
FeO	2.01?
MnO	0.11
MgO	1.38?
CaO	4.18?
Na_2O	3.65?
K_2O	2.90?
H_2O^+	0.36?
CO_2	?
P_2O_5	0.14?
F	*(0.03)
S	?
Others	0.20?
Sum	100.15?
O/F, etc.	0.01?
Sum (corr.)	100.14?
Fe_2O_3TR	3.89?
Fe_2O_3TC	3.93?
ppm	
Ce	45?
Co	7?
Eu	1?
La	26?
Nd	(22)
Sm	4.6?
Tb	(1.2)
Th	14?
Y	13?
Yb	3?

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* Values in parentheses are magnitudes only, not usable values.

UNS – USTAV NEROSTNYCH SUROVIN (Czechoslovakia)

(Contact: RN Dr. Vaclav Zyka, Director, Institute of Mineral Raw Materials, 28403 Kutna Hora-Sedlec, Czechoslovakia).

This institution has prepared several reference materials over the years, apparently in conjunction with related work in East Germany, Bulgaria, Poland and the USSR. Preparation and evaluation of their samples were described by Dempir (1978).

A magnesite, MK, and a glass sand, SS, were produced several years ago. The composition of MK is far removed from those of typical silicate rocks, and that sample is therefore not included in this work. SS was described by the originators (Valcha, 1969) merely as "(T40) from Strelec". The composition values shown in Table 34 are those of Valcha (1972), although some of the trace elements listed by him are not included in this work because too few results were available. As usual, some values have been rounded.

In Valcha (1972), most major and minor constituents were listed as "guaranteed values", being based on results from 13 to 26 laboratories. The trace elements are given merely as such, probably because of limited available data.

In Table 34, the "guaranteed values" are shown without question marks, others with question marks or parentheses. Zinc is shown without question mark, being the only trace element for which the originator's assigned value is based on results from ten or more sources.

The use of the term "guaranteed values" is unique and may suggest a language problem; their publications are generally in English, not in the authors' everyday tongue. In some exchanges, the Kutna Hora staff have referred to values that do not qualify as "guaranteed", merely as "recommended". That practice is in sharp contrast with the usage at USGS, CRPG, ANRT and NIM, all of which reserve the term "recommended" to values established with minimal uncertainty.

A few years after the appearance of the magnesite and glass sand samples, UNS produced a reference sample of kaolinite, KK, described as "the product of kaolinitic weathering of granitic rocks, predominantly of Erzgebirgsgranit and Gebirgsgranit granites at the surface of the Tertiary terrain" near Karlovy Vary. (V. Zyka, personal communication, 1973). The values in Table 34 are from a list kindly provided to this writer by Kutna Hora staff during a visit to their laboratories in 1976. (Our laboratories had contributed data to the evaluation of both KK and SS). The caption on the list is, in Russian, "Attestovanniye soderzhaniya, srok sostavlyeniya aprel' 1976" which translates roughly as "Certified contents, status as of April 1976". (Here we have yet another confusion in terminology.)

More recently, UNS produced a reference sample of fluorite, FM, but that material is not included in this work and GSC laboratories did not participate in the analysis because its composition is far removed from those of silicate rocks.

The essentially perfect summation of sample SS in Table 34 suggests the possibility that the silica value was arrived at by difference, a commendable procedure, as long as all possible impurities have been accounted for.

A persistent problem with reference samples emanating from Eastern Europe is the tendency for the originators merely to list their assigned values with no information on the individual results from which they were derived. In a few cases, maximum and minimum reported results are given, at other times only standard deviations or vaguely defined "limits".

ZGI – ZENTRALES GEOLOGISCHES INSTITUT (East Germany)

Contact: Prof. K. Schmidt, Direktor, ZGI, Invalidenstrasse 44, DDR-104 Berlin, Deutsche Demokratische Republik)

This group, in collaboration with others in several East European countries, has produced a variety of rock and ore reference samples. ZGI appears to be the co-ordinating agency for the entire program.

Table 34. UNS glass sand and kaolinite usable values (originators')

Per cent (dry basis)	Glass Sand SS	Kaolinite KK
SiO_2	99.35	47.06
TiO_2	0.036	0.166
Al_2O_3	0.249	36.77
Fe_2O_3T	0.038	0.98
MnO	0.001?	0.015
MgO	0.007	0.192
CaO	0.030	0.236
Na_2O	0.043	0.032
K_2O	0.057	1.06
H_2O^+		12.75
CO_2		0.17
P_2O_5	0.009?	0.09
F	?	?
S	(0.01)	0.019
L.O.I.	0.169	*0.24
Others	0.01?	0.09?
Sum	100.01?	99.87?
O/F, S etc.	0.01?	0.01?
Sum (corr.)	100.00?	99.86?
ppm		
Be		12?
Cd	2.8?	
Co	0.5?	
Cr	0.8?	9.5?
Cu	8.1?	8.8
Li	4.7?	175?
Ni	2.6?	
Pb	5.7?	120
Rb		160?
Sn		33?
Sr		76?
V	1.4?	
Zn	74	49

* Loss on ignition, less H_2O, CO_2 and S.

Values in parentheses for information only – not usable values

Schindler and Scheutzow (1975) provided an excellent outline of the guiding principles involved in their international program, involving the "CMEA" (Commission for Mutual Economic Aid) countries, and particularly in the work of ZGI itself. They disagreed with the USGS approach, which they regarded as involving three stages, in the evaluation of reference samples: (a): compilation of individual results; (b): (a) plus computation of mean values; (c): (b) plus assignment of recommended values. Their objection was based on the apparent inconsistencies inherent in values derived by subjective considerations. They favoured, instead, a mean of all reported values, after deletion of results shown to be outliers by standard statistical tests. Such an approach, of course, is similar to the "trimmed mean" schemes, as outlined in this paper. The potential weaknesses of such an approach has been illustrated in this work (e.g. in Tables 2, 5 and 6). Even in Table 2 of the Schindler and Scheutzow (1975) paper, there is a striking example of the pitfalls involved in their approach. For cobalt in sample TS, results obtained by a variety of methods, expressed as ppm were: 13, 30, 33, 34, 35, 35, 36, 37, 48.7, 60 and 60. Their statistical tests indicated that only the 13 and the two 60 values were outliers, so they accepted the mean of the remaining eight, i.e. 38.3 ppm. A subjective interpretation would point out that there can be little doubt that the three values rejected were outliers, but what about the 48.7? After eliminating the 13 and the two 60s, the 48.7 was farther removed from its nearest neighbor (37) than the latter was from the opposite extreme (30), so perhaps it should also be deleted. That would leave seven values, ranging from 30 to 37 – a range which would not even encompass the trimmed mean of Schindler and Scheutzow, with a mean of 34.3 and a median of 35. Even if no values had been eliminated, the median of all eleven original values

Table 35. ZGI "international standards" (1975) – usable values (originators')*

Per cent (dry basis)	Basalt BM	Granite GM	Slate TB	Black Shale TS
SiO_2	49.51	73.50	60.24	62.71
TiO_2	1.14	0.21	0.93	0.71
Al_2O_3	16.23	13.55	20.60	15.94
Fe_2O_3	1.60	0.75	0.91	6.72?
FeO	7.28	1.14	5.43	0.66?
MnO	0.14	0.043	0.052	0.04
MgO	7.46	0.38	1.94	1.77
CaO	6.46	1.04	0.33	0.13
Na_2O	4.64	3.76	1.31	0.09
K_2O	0.20	4.74	3.85	4.88
H_2O^+	3.62	0.35	3.82	4.03
CO_2	1.34	0.28	0.13	0.04?
P_2O_5	0.105	0.063	0.095	0.29
F	0.026?	0.067?	0.071?	(0.118)
S	?	?	?	0.22?
Others	0.17?	0.12?	0.26?	2.07?
Sum	99.92?	99.99?	99.97?	100.28?
O/F,S,etc.	0.01?	0.03?	0.03?	0.06?
Sum (corr.)	99.91?	99.96?	99.94?	100.22?
Fe_2O_3TR	9.68	2.02	6.92	7.45
Fe_2O_3TC	9.69	2.02	6.94	7.45?
ppm				
As	14?	4?	11?	
B		14?	92?	85?
Ba	260	330	720	1950?
Be	1.2?	4?	4?	3.5?
†C				1.39(pct)
Ce	27?	60?	115?	
Co	34	3.8	14	38
Cr	120	9.6	76	270
Cs		8?	7?	(12)
Cu	45	13	51	490?
Eu	1.1?	0.56?	1.6?	
Ga	15	14	24	22?
Ge		1.6?	2.5?	
Hf		4.7?	4.8?	
La	9?	35?		(70)
Li	70?	51	115?	43?
Lu	0.4?	0.4?	0.55?	
Mo		1.1?		130?
Nb		17?		
Ni	56	7.4	39	185
Pb	11.5	28	7	33?
Rb	12.5	250	175	220?
Sb	2.0?	0.5?	3.3?	
Sc	34	5?	14	22?
Sm	3.7?	5?	8.7?	
Sn	1.7?	4.5	6?	(5)
Sr	230	135	150	93?
Ta			1.6?	
Th	3?	35?	19?	
U				22?
V	180	11	105	930?
W			3?	
Y	26?	26?	39?	180?
Yb	3.5?	2.9?	4?	(15)
Zn	115	39?	93	89?
Zr	98	150	180	280?

† Non-carbonate carbon

* Slightly modified – see text

(Values in parentheses are magnitudes only, not usable values) would also be 35. Further, with six of the original eleven values clustered symmetrically about 35, any of the modal schemes outlined earlier in this work would have indicated a "best value" of 35. The same value would also have been favoured by Govindaraju's (1980) "preferred mean of central values".

The foregoing paragraph appears to illustrate the futility of uncritical dependence on orthodox statistical treatment. A contrary opinion would hold that the more rigorous statistical treatment would give a better picture of the scatter of reported values. This writer is more inclined to regard each of the outliers (whether three or four) as the result of systematic analytical error, and therefore not a meaningful measurement. For example, how could two analysts determine cobalt spectrophotometrically (method otherwise unspecified), with one finding 13 ppm, the other 35? Similarly, would two different determinations by atomic absorption yield results as disparate as 30 and 60 ppm? A plausible reply to the first question would be: if the low result represented an incomplete decomposition of the sample. Similarly, the second question might be answered as: perhaps the higher result was the result of failure to correct for background (or blank?). Unfortunately, neither of the two replies can be confirmed or contradicted as long as contributing laboratories do not report details of their methodology. However, any knowledgeable analyst who attempts to evaluate disparate analytical data, should be able to recognize values that can result from failure of the contributors to recognize common pitfalls. Incidentally, similar reasoning is equally applicable to the two other examples cited in their Table 2 by Schindler and Scheutzow (1975).

Although the foregoing paragraphs appear to be highly critical of the evaluation scheme of Schindler and Scheutzow, there is no intention in this work to denigrate their paper. They presented a strong and convincingly stated case for the need for the production of many reference materials of varied compositions. Perhaps the most intriguing of their ideas was the proposal to prepare blends of various reference samples. They even indicated that the selection of materials to use as "standards" had that end in mind. They showed data to support the view that analyses based on such "blended standards" tended to give superior results, relative to analyses based on individual reference materials. That view is compatible with this writer's opinion that no single reference material should be depended upon by itself. For best results, a group of at least four reference samples of varied composition should be used together or even as blends, whether in calibrations, in controlling reliability in regular analysis or in testing new methods.

In an advertising brochure (ZGI, undated) nine reference materials were presented as six "international standard samples" and three "national standard samples", with the implication that the latter would eventually be promoted to the "international" level. For purposes of this work, the samples are considered under those two categories.

ZGI "international standards"

The six "international" samples are AN (an anhydrite), BM (a basalt), GM (a granite), KH (a limestone), TB (a slate) and TS (a black shale). AN and KH are of compositions that differ greatly from those of silicate rocks, and are therefore not included in this work.

Progress in the development of these materials has been reported in a series of papers (Grassmann, 1964; Schindler, 1966; Grassmann, 1966; Friese and Grassmann, 1967; Schindler, 1972; Grassmann, 1972). The last two references gave fairly comprehensive listings of means and recommended values for all of these samples, except TS, for which only preliminary values were listed. The values shown in Table 35 are based on the certificate issued with each sample (ZGI, 1975a, b, c, d), which list "Attestierte Gehalte", or "certified contents" (author's translation from German), as of 15 March, 1969 for BM, GM and TB, and as of 15 August, 1975 for TS.

BM is described as a basalt of apparently Devonian age, a greenish grey rock, intermixed with narrow, calcite-filled fissures, originating in a quarry at Mellenbach, near Grossbreitenbach, in the Suhl region.

GM is from the "Red Granite" quarry in Meissen, in the Dresden region. It belongs to the syenite-granodiorite massif, a post-Variscan intrusion in the Elbe Valley zone. The material is a reddish grey, coarse-to moderately coarse-grained rock, with a similar proportion of fine-grained inclusions.

TB comes from the underground workings of fractured slate at Bohlscheiben, near Blankenburg, in the Gera region. The slate appears to be megascopic and very uniform, with the exception of a few streaks.

TS is a black, highly coloured clayey rock, in which the original sedimentary stratification structure (interbedding with clay stone and quartz layers) became strongly overprinted by tectonic deformation. It comes from a trench on the road between Schwarzburg and Katzhutte, south of the Orsteil shale workings of the Menselbach-Schwarzmuhle Community, in the Suhl region.

There are a few contradictions between the certificate values for BM, GM and TB and those quoted in the descriptive papers (Grassman, 1972; Schindler, 1972). Although the certificates are dated October 1975, the values listed in them are as of March 1969. The papers are from 1972, so it is difficult to distinguish which figures represent the more recent evaluation. Inquiries directed to the originators have failed to produce an elucidation.

The certificates for BM, GM and TB show all values as "certified". However, some of the trace-element values were based on results from fewer than 10 sources. Such values are shown with question marks in Table 35. The same rule was applied to TS. However, the certificate for that sample also includes a table of "uncertified contents". Values in that table representing data from five or more sources are given in Table 35 with question marks; those based on fewer than five sources are shown in parentheses.

The acceptable summations and good iron-oxide compatibilities in Table 35 tend to support the validity of the ZGI's assigned values. However, the questions raised earlier regarding their method for deriving "best values" should not be forgotten. Some observations made in GSC laboratories have also cast doubt on the reliability of a few ZGI values. Although we have done considerable work on the ZGI samples, none of our results have been used in their evaluation – as far as we know.

ZGI "national standards"

The three samples shown in the advertising brochure (ZGI, undated) under this category are FK, GnA and SW.

No information is available to this writer regarding sample FK, other than the fact that it is a "potash feldspar sand". The values shown in Table 36 are from a single sheet supplied with the sample (ZGI, 1973), except those for trace elements, which are from Schindler and Scheutzow (1975). All FK values in Table 36 are therefore shown with question marks.

The documents supplied with GnA (ZGI, 1977a) and SW (ZGI, 1977b) give no information about the backgrounds of the samples, in striking contrast with the more detailed information on the certificates for BM, GM and TB. We know from the advertising brochure that GnA is a greisen and SW a serpentinite.

The documents for GnA and SW are both dated "as of 9/77". Each contains three tables: certified values, uncertified values based on results from six or more sources, and uncertified values based on fewer than six results. In Table 36, question marks are shown with the certified values based on results from fewer than 10 sources and on the uncertified values based on six or more sources. All values listed by ZGI as uncertified, based on results from fewer than six sources, are shown in Table 36 in parentheses.

The high total for SW in Table 36 is not unusual with ultrabasic samples, and may be the result of calculating most constituents as oxides, although certain elements (notably nickel) may occur partially as free metal.

The iron-oxide compatibility test does not apply in this case because the certificates list Fe_2O_3T for all three samples, as well as FeO for GnA and SW. The Fe_2O_3 values in Table 36 were computed by difference.

In both Tables 35 and 36, some listed values have been rounded to conform with the other samples described in this paper.

As mentioned earlier ZGI acts as co-ordinator of the Eastern European ("CMEA") collaborative program on geological reference materials. Unfortunately, comparatively little is published in the "outside world" regarding that work. In addition to the ZGI, UNS and IGI (described later in this report) samples, mention has been made occasionally of a few others (possibly including the Bulgarian granite, G-B) either in preparation or proposed. They involve a gabbro, a nepheline syenite, a fire clay, a monzonite, a slate, a skarn and a kieselguhr. Belyaev and Sobornov (1981) listed some samples in their work with which this writer was not familiar. They may be among those referred to above.

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(Contact: Prof. A.A. Kukharenko, Department of Mineralogy, Leningrad State University, Leningrad V-164, USSR).

The one sample from this source was originally described by Kukharenko et al. (1968) as "Khibiny-Generalnaya", a nepheline syenite. When the sample first arrived at the GSC with a request for analytical data, it bore no identification number, and was therefore designated by us as "NS-1". As far as can be learned from the limited literature, the sample was possibly a composite from a relatively large area. It may not even have been intended as a reference material. However, a generous quantity of material was provided, and considerable analytical data were reported to Leningrad. No acknowledgment was received, but the subsequent publication (Kukharenko et al., 1968), unlike later reports from Eastern Europe countries, listed individual results from some 21 laboratories – not including the GSC.

In some earlier papers in this series (Abbey, 1972, 1973, 1975b, 1977a), "adjusted means" were listed as usable values. These were the means of values remaining after rejecting the 20 per cent of the originally reported results that were farthest removed from the overall mean. Some of the values thus deduced appeared unsatisfactory and yielded a rather high summation. It was therefore decided to apply the select laboratories approach in more recent work (Abbey, 1980), although that scheme had never before been applied to a single-sample operation. The new approach brought about a general slight lowering of most of the usable values, the summation being reduced from 100.34 to 100.06. The most recently derived values are shown in Table 37.

Table 36. ZGI "national standards" (1975) – usable values (originators')*

Per cent (dry basis)	Feldspar Sand FK	Greisen GnA	Serpentine SW
SiO_2	88.15?	71.45	39.05
TiO_2	0.059?	0.023	0.016
Al_2O_3	6.22?	14.7	0.68
Fe_2O_3		1.70	5.17?
FeO		3.80	2.0?
MnO	0.006?	0.166	0.083
MgO	0.16?	0.033	38.5
CaO	0.12?	0.61	0.18
Na_2O	0.25?	0.08	0.013
K_2O	4.15?	2.63	0.014?
H_2O^+	0.41?	1.8?	13.6
CO_2	0.025?	(0.04)	0.29?
P_2O_5	0.075?	0.016?	0.026?
F		3.36	(0.007)
S		(0.016)	(0.014)
Others	0.02?	1.10?	0.68?
Sum	99.90?	101.52?	100.32?
O/F,S,etc.	?	1.42?	0.01?
Sum (corr.)	99.90?	100.10?	100.31?
Fe_2O_3TR	0.26?		
Fe_2O_3TC		5.92	7.40?
ppm			
Ag		(0.8)	(0.4)
As		(47)	(3.1)
B		20?	(39)
Ba		(47)	(21)
Be		5?	
Bi		220?	(36)
Ce		(86)	
Co		(2.1)	100
Cr		14?	2500
Cs		46	(0.28)
Cu		18	7
Ga		60	(1.3)
Ge		(6.5)	
La		(33)	
Li		2200	
Mo		100	
Nb		90?	
Ni		(5.1)	2200
Pb	17?	20?	19?
Rb	135?	2000	(1.3)
Sc		9?	(11.5)
Sn		1900	6.4
Sr		(19)	(17)
Ta		(29)	
Th		40?	(17)
U		22?	(1.6)
V		(2)	19?
W		520?	(0.47)
Y		(22)	
Yb		(8)	
Zn	12?	76	58
Zr	70?	70?	

* Slightly modified – see text

(Values in parentheses are mere magnitudes, not usable values

Table 37. LEN syenite – usable values (compiler's)

Per cent (dry basis)	Nepheline Syenite NS-1
SiO_2	53.22
TiO_2	1.05
Al_2O_3	21.31
Fe_2O_3	2.31
FeO	1.60
MnO	0.18
MgO	0.64
CaO	1.70
Na_2O	9.85
K_2O	6.52
H_2O^+	0.66
CO_2	0.14?
P_2O_5	0.28
F	0.14
S	0.01?
Others	0.53?
Sum	100.14?
O/F,S,Cl	0.08?
Sum (corr.)	100.06?
Fe_2O_3TR	4.10
Fe_2O_3TC	4.09
ppm	
Ba	1200
Be	6?
Ce	185?
Cl	500?
Co	8?
Cr	10?
Cs	3.3?
Cu	8?
Dy	2?
Er	2?
Ga	24?
Ge	1?
La	105?
Li	21?
Mo	2?
Nb	195?
Nd	71?
Ni	7?
Pb	7?
Pr	20?
Rb	210
Sm	10?
Sn	3.5?
Sr	1150
Ta	11?
Th	9?
U	4?
V	51
Y	17?
Zn	70?
Zr	720

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(Contact: Prof. L.V. Tauson, Institute of Geochemistry, Academy of Sciences of the USSR (Siberian Branch), P.B. 701, Irkutsk-33, USSR)

Three samples were originally received at the GSC laboratories, with no background information, other than the sample identifications: trap 2001, gabbro 2003 and albitized granite 2005. Our laboratories contributed a large quantity of data, which were forwarded to the originators, but were never acknowledged.

To this writer's knowledge, no compilation of analytical data on these samples has ever been published – not surprisingly, as that seems to be the policy of the group from the "Comecon" or "CMEA" countries. However, Tauson et al. (1974) reported a set of "attested" (certified) and some uncertain values for three samples: trap ST-1A, gabbro SGD-1A and albitized granite SG-1A. On comparing those values with results obtained in our own laboratories, one could not help but conclude that the three samples were the same as those identified earlier as 2001, 2003 and 2005. As pointed out earlier (in the section of this report on "Comparisons"), Tauson et al. (1974) not only gave no information on how their values were deduced, but gave no explanation of why the sample identifications were changed. Some of the other problems with these samples have also been mentioned in the section on Comparisons, so there is no need to detail them here.

Table 38 lists the values given by Tauson et al., except for uranium in ST-1A and lanthanum in SG-1A, for which elements the values are those recommended by Lontsikh et al. (1979). Those authors used the results of Abbey and Govindaraju (1978), as well as a few additional results from Soviet laboratories to adjust the recommended values for the above elements. Unfortunately, there was some confusion in the paper by Lontsikh et al. (1979). Their text stated that original data indicated 41 ppm La in ST-1A, but the additional data would bring that value down to about 30 ppm. However, their Table 1 showed 14 ppm La in ST-1A, the same value given as "attested" by Tauson et al. (1974). On the other hand, 41 ppm La is shown for SG-1A, both by Lontsikh et al. and by Tauson et al. It is thus possible that there was a misprint in the allusion to sample ST-1A, a possibility supported by the similarity between the Cyrillic capital letters for T and G, the latter resembling the Greek "gamma".

In the same paragraph, Lontsikh et al. suggested that the uranium content of ST-1A be 0.7 ppm, rather than 1 ppm, as recommended by Tauson et al. In this case, there is no contradiction with the tabulated value.

Careful examination of the data in the paper by Lontsikh et al. (1979) will suggest that the values "attested" for these three samples by Tauson et al. (1974) may well have been based on far fewer than the ten separate determinations for each constituent that this writer considers a safe minimum for derivation of "unquestioned" values.

The question marks in Table 38 are placed against the values shown by Tauson et al. in parentheses. They pointed out the potential usefulness of each sample in the analysis of particular types of rocks, but perhaps more importantly, the three samples show a very good gradation in the contents of various constituents and should therefore be very useful in calibrations. As mentioned earlier, the unquantifiable uncertainties in assigned concentration values mitigate against the use of one reference material alone; a set of three with nicely graded compositions can be more dependable. On the other hand, the limitations of these particular three should not be forgotten.

Table 38. IGI rocks – usable values (originators')

Per cent (dry basis)	Albitized Granite SG-1A	Gabbro SGD-1A	Trap ST-1A
SiO_2	73.36	46.39	49.12
TiO_2	0.072	1.71	1.82
Al_2O_3	13.84	14.88	14.23
Fe_2O_3	0.68	3.86	3.92
FeO	1.41	6.86	10.26
MnO	0.19	0.17	0.21
MgO	0.054	7.09	5.74
CaO	0.14	10.97	10.20
Na_2O	5.46	2.82	2.49
K_2O	4.14	2.96	0.69
H_2O^+	0.21	0.83	0.97
CO_2	0.07?	0.13	0.099
P_2O_5	0.013	1.01	0.21
F	0.30	0.12	0.032?
S	0.017	0.02	0.068
Others	0.50?	0.63?	0.31?
Sum	100.46?	100.45?	100.37?
O/F,S,Cl	0.13?	0.07?	0.06?
Sum (corr.)	100.33?	100.38?	100.31?
Fe_2O_3TC	2.25	11.48	15.32
ppm			
B	10	16	15
Ba	19	1300	290
Be	11	2	1
*C	420?	280	360
Ce	67?	150	22?
Cl		220?	430?
Co	1.4	40	46
Cr	12	52	140
Cs	12	4	0.9
Cu	31	68	220
Dy	5?	4?	4?
Er	7?	2.8?	2?
Eu	0.5?	6	3
Ga	40	19	16
Ge	3.3	1.5	1.6
Ho	1?	0.5?	0.8?
La	30?	78	14
Li	390	14	14
Mo	1.3	1.5	1.8
Nb	380	8	8
Nd	18	66?	9
Ni	11	50	90
Pb	230	18	6
Pr	3?	10?	2
Rb	1100	73	16
Sb	1.3?	1?	1
Sc	5	27	43
Sm	7	17	4
Sn	11	3.7	3.5
Sr	20	2300	270
Ta	26	1.1	1.2
Th	120	9	3?
U	63	4?	0.7?
V	5	240	320
W	2.3		
Y	69	30	30?
Yb	6	2.9	4
Zn	270	120	150
Zr	720	240	130
†RE_2O_3	280?	460?	120?

* Non-carbonate carbon (as C)

† Total rare-earth oxides

Other IGI samples

This paper has alluded repeatedly to problems of communication with reference sample programs in the USSR and other Eastern European countries. The samples discussed in this section provide yet another example of limited background information and incomplete compositional data.

Belyaev and Sobornov (1981) mentioned the following samples (otherwise not referred to in this paper) as originating with IGI: alaskite granite SG-2, nepheline syenite SNS-2, nepheline ore SNS-1, dolomitic limestone SI-1, loparite concentrate SVT-16A, Ta-Nb concentrate SVT-17, calcareous mud SDo-3, volcanic terrigene mud SDo-2, terrigene clay SDo-1, aleurolite SA-1, and bauxites SB-1 and SB-2. As usual, no information was given about those samples, nor was there any hint of their compositions beyond the potassium, uranium and thorium contents under study. Some of the same samples were also referred to by Lontsikh and Parshin (1979), but they were more concerned with the range of values reported by collaborating analysts than with background information about the samples. Once more, it should be noted that the designation SDo-1 duplicates that of a USGS shale, but no attempt has been made in this work to resolve the discrepancy because so little information is available about both samples.

Although far from comprehensive, more information was gleaned from a paper by Sidorovski et al. (1976). By combining Tables 5 and 6 from Sidorovski et al. with Table 1 from Lontsikh and Parshin (1979) and Table 1 from Belyaev and Sobornov (1981), it was possible to deduce the following information (restricting ourselves to samples of types included in this work):

> SA-1 is an aleurolite rock. SB-1 and SB-2 are bauxites. SG-2 is an alaskite granite. SNS-1 is a nepheline ore. All that can be learned about the origin of any of these samples is that they were issued by IGI. No information was provided about their geological background. Table 39 gives a limited number of reportedly "attested" values for these five samples. However, since our information is so incomplete, it was decided to list those values "for information only", not to incorporate them in the "concentration ladders" of Part III, and hence not to consider them "usable". The low summations in Table 39 are not surprising.

OTHER SAMPLES FROM THE USSR

In the course of the search for additional information on IGI samples, it was noted that Sidorovski et al. (1976) gave some compositional data on three samples which appear to emanate from Soviet sources other than IGI. Lontsikh and Parshin (1979) described them as: SP-1, a "black earth" from Kursk; SP-2, a "sod-podzol" from [near?] Moscow; and SP-3, a "light chestnut colored" soil from [near?] the Caspian Sea.

Table 40 lists the compositions of the samples, as reported by Sidorovski et al. As was the case with the additional IGI samples, the figures in Table 40 are not considered as usable values because of the limited amount of available information.

Table 39. Other IGI samples – information values (originators'?)

Per cent (dry basis?)	Aleurolite Rock SA-1	Bauxite SB-1	Bauxite SB-2	Alaskite Granite SG-2	Nepheline Ore SNS-1
SiO_2	60.6	2.38	7.38	72.1	40.18
TiO_2	0.95	2.22	3.06	0.23	0.24
Al_2O_3	18.2	55.4	48.6	14.0	28.5
Fe_2O_3C		20.0	23.9?		1.66
FeO	4.8	2.2	3.89?	1.08	1.43
MnO	0.042			0.018	0.04
MgO	2.2	0.14	0.39?	0.21	1.01
CaO	0.48	1.93	0.39?	0.73	7.13
Na_2O	2.3			2.5	12.2
K_2O	3.45			7.2	3.3
H_2O^+	4.1	10.9	11.7?	0.35?	1.9
CO_2	?	?	?	?	?
P_2O_5	0.18	0.69	0.22	0.08	0.51
F	0.058?			0.026?	
S	0.088	0.33	0.028		0.084
Others	0.27?	?	?	0.31?	?
Sum	97.72?	96.19?	99.56?	98.84?	98.18?
O/F,S,etc.	0.07?	0.16?	0.01?	0.01?	0.04?
Sum (corr.)	97.65?	96.03?	99.55?	98.83?	98.14?
Fe_2O_3TR		22.4	28.2		3.25
ppm					
B	87			55	
Ba	910			1900	
Be	2.8			1.4	
Co	21			3.2	
Cr	96			14	
Cs	6.3			2.8	
Cu	41			34	
Ga	21			14	
Ge	1.7?			1.8?	
Li	58			4.3	
Mo	1.1?				
Nb	15?			2.9?	
Ni	61			11	
Pb	21			23	
Rb	120			150	
Sc	19			3.1	
Sn	3.1			1.8	
Sr	170			370	
Th	10			12	
Y	170			28	
Yb	32				
Zn	120			24	
Zr	220			160	

IGGE - INSTITUTE OF GEOPHYSICAL AND GEOCHEMICAL EXPLORATION (CHINA)

Contact: Xie Xuejing, Deputy Director, Institute of Geophysical and Geochemical Exploration, Hubei Province, Lang Fang County, (via Ministry of Geology, Beijing), China.

Yang et al. (1981) described the preparation, analysis and evaluation of a suite of eight sediment samples for use as reference materials. The program was organized jointly by the IGGE and the Institute of Analytical Techniques of the Chinese Academy of Geological Sciences, with the active initial participation of seven provincial geological bureaus. Subsequently, about 30 other Chinese laboratories contributed varying quantities of data.

The samples, designated GSD-1 to GSD-8, are stream sediments of varying compositions. The usable values were derived by a "polyparametric" method. Outlying values were first eliminated on the basis of a simple statistical test. Of the remaining values for each constituent, five "central measures" were computed, as well as standard deviation, coefficient of variation, skewness and kurtosis. The "central measures" were the arithmetic mean, geometric mean, preferred mean (the mean after eliminating values beyond one standard deviation of the arithmetic mean), median and mode. A "preferred mean of central values" was then computed, as well as a similar parameter for each of the methods used for the particular constituent, and the mean of all of those measures taken as usable value.

Table 40. USSR soils – information values (originators'?)

Per cent (dry basis?)	Soil SP-1	Soil SP-2	Soil SP-3
SiO_2	69.53	78.33	65.72
TiO_2	0.75	0.84	0.73
Al_2O_3	10.37	9.57	12.61
Fe_2O_3T	3.81	2.93	4.91
MnO	0.077	0.07	0.092
MgO	1.02	0.77	1.95
CaO	1.63	0.81	2.85
Na_2O	0.80	1.15	1.16
K_2O	2.29	2.47	2.51
H_2O^+	?	?	?
CO_2	?	?	?
P_2O_5	0.17	0.075	0.21
F	0.028	0.021	0.036
S	0.069	0.061	0.028
Others	0.18?	0.30?	0.18?
Sum	90.72?	97.40?	92.99?
O/F,S,etc.	0.05?	0.04?	0.03?
Sum (corr.)	90.67?	97.36?	92.96?
ppm			
B	53	43	71
Ba	430	530	470
Be	2	1.5	2.2
Co	10	10	14
Cr	82	840	140
Cs	3.8	2.4?	5?
Cu	22	17	30
Ga	10	8.5	13
Li	20	16	24
Mo	1	1	1.1
Nb	17	22	18
Ni	33	25	56
Pb	16	14	16
Rb	84	72	85
Sc	12	9.4	14
Sn	3.9	2.8	4.9
Sr	130	120	160
Y	77	64	11
Yb	39	27	28
Zn	52	45	73
Zr	450	540	300

The Chinese method is in many ways similar to those used in recent work by Steele et al. (1978), Steele and Hanson (1979) and by Govindaraju (1980, 1982), with the significant difference that the Chinese authors did not introduce any subjective judgment.

The originators' usable values for the eight samples are shown in Table 40A, without the uncertainty limits which they reported (Yang et al., 1981), in keeping with the policy enunciated earlier in this paper. Similarly, many of the trace-element values have been rounded. It is apparent from the original report that trace elements were intended to be of prime importance with these samples.

Several interesting points concerning major and minor constituents are discernible in Table 40A. Thus all ferrous and ferric values are shown as uncertain. No raw data for those constituents were quoted, although detailed figures were shown for most other constituents. It was mentioned that few results had been available for Fe'' and Fe'''. The persistent discrepancy between the two values for total iron could be interpreted in two ways. Normally, such discrepancy suggests questionable validity in the derivation procedure. In this case, however, a different explanation may be more likely. We know that few results were available for ferrous and ferric. We also know that Fe_2O_3TC is lower than Fe_2O_3TR in all eight samples. Such a bias could result from a negative error in a significant number of the contributed ferrous results. In the absence of the raw data for the two forms of iron, it is not possible to know for certain what is the more likely cause of the total iron incompatibility. However, the nearly linear relationship between the "total-iron discrepancy" and the FeO concentration in the various samples tends to support the probably systematic negative error in ferrous determination as the more likely source of the discrepancy.

The relatively high values for L.O.I. are also shown as uncertain, again with no listing of raw data. It is possible that water, carbonate and non-carbonate carbon, organic matter, sulphur, etc. may be present, but no mention was made of such constituents in the original report.

GSJ – GEOLOGICAL SURVEY OF JAPAN

(Contact: Dr. Atsushi Ando, Geochemical Research Section, Geological Survey of Japan, 135 Hisamoto-cho, Kawasaki-shi, Japan.)

There has been no dearth of information concerning the granodiorite and basalt reference samples produced by this group.

Ando (1967) first introduced the granodiorite JG-1, indicating that it was collected from Sori, Gunma-ken, about 100 km north of Tokyo. A year later, JB-1 was described as a tinanaugite-olivine trachybasalt from Myokanji-toge, 7 km north-northwest of Sasebo City, Kyushu (Ando, 1968). GSC laboratories contributed large quantities of analytical data to the evaluation of both samples, second only in numbers to those reported by the originating institution.

Ando et al. (1971) published a compilation of data on the two samples, also including "consensus means", defined as "arithmetic mean of the analytical values within 2-sigma [of the overall mean]" for major and minor constituents. An early version of the select laboratories method was applied to the 1971 data to produce a limited number of usable values (Abbey, 1975b). A second, more comprehensive compilation appeared three years after the first (Ando et al., 1974). The data from the latter compilation were used in a second round of calculations by the select laboratories method, yielding many additional values for trace elements, among other things.

Problems arose in the second round calculations for JB-1. The usable value for silica increased from 52.49 to 52.72 per cent, the corrected summation going from 100.10 to 100.31. The change in summation may have been the result of the increased silica value, or from the increased number of trace elements for which there were sufficient reported results to justify listing usable values. The value for silica was therefore listed (Abbey, 1977b) as 52.60, which was the mean of the two computed values, as well as being the "adjusted mean" of available results in the second compilation – i.e. the mean of reported values remaining after elimination of the 20 per cent of the values that were farthest removed from the overall mean. Because of the uncertainty in the highly subjective decision to change the silica value, the value is listed in Table 41 with a question mark.

Table 40A. IGGE (China) sediments – usable values (originators')

Pct	GSD-1	GSD-2	GSD-3	GSD-4
SiO_2	58.48	69.94	71.34	52.68
TiO_2	0.98	0.23	1.07	0.90
Al_2O_3	14.86	15.75	12.09	15.72
Fe_2O_3	4.59?	1.23?	5.68?	4.51?
FeO	2.33?	0.57?	0.72?	1.18?
MnO	0.12	0.03	0.05	0.11
MgO	4.15	0.21	0.68	1.01
CaO	4.64	0.31	0.25	7.48
Na_2O	3.49	3.10	0.32	0.29
K_2O	2.78	5.18	2.44	2.16
L.O.I.	2.4?	2.96?	4.67?	12.74?
P_2O_5	0.34	0.04	0.14	0.11
F	0.09	0.20	0.03	0.07
Others	0.32?	0.22?	0.21?	0.19?
Sum	99.57?	99.97?	99.69?	99.15?
O/F	0.04	0.08	0.01	0.03
Sum (corr)	99.53?	99.89?	99.68?	99.12?
Fe_2O_3TR	7.34	1.90	6.53	5.90
Fe_2O_3TC	7.18?	1.86?	6.48?	5.82?
ppm				
Ag	0.05?	0.07	0.59	0.085
As	2.0	6.4	17.5	19.5
Ba	950	190	620	450
Be	3.0	17	1.5	2.3
Bi	0.66	1.6	0.81	0.67
Cd	0.08	0.06	0.10	0.19
Co	21	2.8	12	18
Cr	195	12.5	87	81
Cu	22	4.9	175	37
La	45	87	41	44
Li	30	100	33	51
Mo	0.74	2.0	93	0.82
Nb	36	96	16	18.5
Ni	76	5.5	26	40
Pb	24	31	41	31
Rb	115	480	78	130
Sb	0.2?	0.5?	5.6	1.9
Sn	2.8	29	3.0	4.0
Sr	520	27	91	140
Th	26	67	8.9	14.5
U	4.3	15.5	1.8	2.3
V	120	16	120	120
W	1.0	24	5.0	2.4
Y	22	67	22	27
Zn	79	44	52	100
Zr	310	460	220	190

Pct	GSD-5	GSD-6	GSD-7	GSD-8
SiO_2	56.44	61.22	64.70	82.92
TiO_2	0.90	0.78	0.75	0.61
Al_2O_3	15.47	14.17	13.46	7.70
Fe_2O_3	4.53?	4.04?	4.75?	1.56?
FeO	1.10?	1.53?	1.48?	0.54?
MnO	0.15	0.13	0.09	0.04
MgO	0.96	2.98	3.08	0.26
CaO	5.30	3.85	1.66	0.26
Na_2O	0.41	2.32	1.23	0.50
K_2O	2.04	2.43	3.49	2.75
L.O.I.	11.41?	5.38?	4.20?	2.44?
P_2O_5	0.14	0.23	0.19	0.03
F	0.06	0.07	0.09	0.02
Others	0.24?	0.26?	0.29?	0.17?
Sum	99.15?	99.39?	99.46?	99.80?
O/F	0.03	0.03	0.04	0.01
Sum (corr.)	99.12?	99.36?	99.42?	99.79?
Fe_2O_3TR	5.83	5.85	6.50	2.20
Fe_2O_3TC	5.75?	5.74?	6.39?	2.16?
ppm				
Ag	0.37	0.35	1.1	0.064
As	74	13.5	83	2.5
Ba	440	330	730	490
Be	2.4	1.6	2.7	2.0
Bi	2.4	5.0	0.68	0.20
Cd	0.82	0.42	1.0	0.079
Co	19.5	25	21	3.7
Cr	70	190	120	7.3
Cu	135	380	37	4.0
La	47	41	45	31
Li	45	40	32	13.5
Mo	1.1	7.8	1.4	0.52
Nb	19.5	12.0	16.5	35
Ni	34	79	54	3.0
Pb	115	28	350	21
Rb	120	105	145	130
Sb	4.1	1.1?	2.7	0.22?
Sn	4.6	2.8	5.3	9.2
Sr	200	260	220	52
Th	15.5	9.3	12	13.5
U	2.4	2.2	3.2	3.1
V	110	140	96	26
W	3.2	25	5.6	1.9
Y	26	21	23	17
Zn	240	145	240	44
Zr	220	170	165	490

A possible source of the problem with the silica values in JB-1 is the relatively high H_2O^- content. Because some analysts do not report that easily determined but possibly variable constituent, a significant error may thereby be introduced in the results for major constituents.

Ando (1975) listed a set of "estimated values" for "minor elements" (mainly traces) in JB-1 and JG-1. Those values were given priority over the ones deduced by the select laboratories method, in all subsequent publications – with some exceptions. The exceptions were those cases where, in this writier's opinion, the number of reported results were insufficient to establish firm values. The constituents so affected are shown with question marks or parentheses in Table 41, the choices being based on a combination of the number of reported results and the number of different analytical methods involved. Ando's estimates were based largely on arithmetic means, but some subjective judgment was involved in a few cases where results from particular analytical techniques were favoured.

Table 41. GSJ rocks – usable values

Per cent (dry basis)	Basalt JB-1	Granodiorite JG-1
SiO_2	52.60?	72.36
TiO_2	1.34	0.27
Al_2O_3	14.62	14.20
Fe_2O_3	2.36	0.37
FeO	6.02	1.62
MnO	0.15	0.06
MgO	7.76	0.76
CaO	9.35	2.17
Na_2O	2.79	3.39
K_2O	1.42	3.96
H_2O^+	1.01	0.54
CO_2	0.18?	0.08?
P_2O_5	0.26	0.09
F	0.039?	0.049?
S	(0.01)	(0.00)
Others	0.29?	0.15?
Sum	100.20?	100.07?
O/F,S,Cl	0.03?	0.02?
Sum (corr.)	100.17?	100.05?
Fe_2O_3TR	9.01	2.16
Fe_2O_3TC	9.05	2.17
ppm		
Ag	0.06?	0.05?
As	(2)	(0.3)
B	12?	6?
Ba	490	460
Be		(3)
Ce	67?	43?
Cl	175?	59?
Co	39	6.4
Cr	400	53
Cs	1?	10?
Cu	56	4
Dy	4?	3.2?
Er	(2.3)	
Eu	1.5?	(0.7)
Ga	17?	15?
La	36?	22?
Li	11?	94?
Lu	0.3?	
Mo	20?	2?
Nd	21?	
Ni	135	8.2
Pb	11.5	26
Rb	41	185
Sm	4.8?	4.6?
Sn	2?	4?
Sr	440	185
Th	9?	13.5
U	1.8	3.3
V	210	24
Y	26?	31?
Yb	2.1?	1.5?
Zn	84	40
Zr	155	110?

(Values in parentheses are magnitudes only, not usable values.)

Note: All trace elements, plus Na_2O, K_2O, F and S show originators' values. Remaining major and minor constituents show compiler's values. See text for explanation.

Table 42. Later GSJ rocks – information values (compiler's)

Per cent (dry basis)	Andesite JA-1	Basalt JB-2
SiO_2	63.76	53.38
TiO_2	0.92	1.26
Al_2O_3	15.50	14.68
Fe_2O_3	2.42	3.32
FeO	4.43	9.99
MnO	0.16	0.22
MgO	1.60	4.63
CaO	5.70	9.83
Na_2O	3.92	2.06
K_2O	0.84	0.44
H_2O^+	0.42	0.22
CO_2	?	?
P_2O_5	0.16	0.09
F	?	?
S	?	?
Others	0.00?	0.00?
Sum	99.83?	100.12?
O/F,S,etc.	0.00?	0.00?
Sum (corr.)	99.83?	100.12?
Fe_2O_3TR	7.34	14.42
Fe_2O_3TC	7.34	14.42
ppm		
Co	12	12
Cu	36	
Ni	0.1	12
Pb	0.4	1.5

In another report, Ando et al. (1975) listed "recommended" values for sodium, potassium, rubidium and strontium in the two samples. In this case, they found that, for the latter two elements, the means of results by isotope dilution and mass spectrometry were very close to the means of all results after removal of those that differed from the overall mean by more than one standard deviation (i.e. the "preferred mean" of Govindaraju). They therefore recommended values somewhat closer to the ID-MS results. For sodium and potassium, they recommended the "preferred mean". The values thus recommended for the four elements are shown in Table 41, except that those for rubidium and strontium have been rounded to a slight extent.

Information on two later GSJ samples has been less plentiful. Kato et al. (1978) reported three separate essentially classical analyses for major and minor constituents in JA-1, an andesite, and JB-2, another basalt. A limited number of results by other methods were also reported for sodium, potassium and a few trace elements. The values shown in Table 42 (all merely information, not usable, values) are the medians of those listed by Kato et al., after conversion to the dry basis.

With some justification, questions can be raised regarding some decisions arrived at in this work, concerning the choice between originators' vs. compiler's values. With the GSJ samples, the originators' values, where available, have been favoured over those derived by the select laboratories method. With USGS samples, the opposite decision prevailed. The apparent contradiction is debatable, but the following points may serve to support the actual decisions:

(a) The first two GSJ samples were introduced in 1967 and 1968. Assigned values, as far as they went, became available by 1975 with explanations of how they were deduced. Unfortunately, none were assigned for major and minor constituents (except sodium and potassium), so the listed values for such components are based on the select laboratories method. The summation and iron-oxide compatibility tests therefore cannot be applied to the originators' recommended or estimated values. Thus there remains some doubt about the validity of the decision to use the originators' values.

(b) With the USGS materials, the situation was far worse. The discrepancies in their values for USGS II are clearly indicated in Table 3. With USGS III, the originators had not published assigned values 16 years after data on some of the samples first appeared in the literature. A set of values was provided to this writer for USGS IV (see Table 16), but some shortcomings in those figures have been pointed out in the text. Further, USGS has never published an explanation of how their "recommended", "average" and "magnitude" values are arrived at, nor what constitutes the distinction between them.

NIES – NATIONAL INSTITUTE FOR ENVIRONMENTAL STUDIES (Japan)

(Contact: Kensaku Okamoto, National Institute for Environmental Studies, P.O. Yatabe, Ibaraki 305, Japan)

The one sample of geological interest prepared by this group was described by Iwata et al. (1981) as a pond sediment, collected from the Sanshiro-ike pond at the University of Tokyo, and consisting of "Kanto Loam", probably originating from old volcanic ash. The originators did not assign a designation for the sample; it is therefore referred to in this work as PSJ-1 (for pond sediment, Japan). They emphasized the differences in composition between PSJ-1 and such river sediment material as NBS-1645.

Iwata et al. gave excellent background information on the preparation and analysis of the sample, but pointed out that their values (see Table 43, where they have been re-cast in conventional rock-analysis form) "...have not been certified yet...", presumably because of the limited quantity of analytical data, all of which evidently came from the Chemistry Department of the University of Tokyo. The numbers in Table 43 are therefore considered "information values", not "usable". Work is apparently underway, at this writing, leading to eventual "certification". On the basis of the available data, PSJ-1 will likely develop into a highly useful material.

MRT – MINERAL RESOURCES, TANZANIA

(Contact: Commissioner, Mineral Resources Division, P.O. Box 903, Dodoma, Tanzania)

The only reference material produced by this group, tonalite T-1, is no longer available and no replacement is expected. It is included in this work because many laboratories may still have some on hand. Burks and Palliser (1961) stated that it was "...chosen as a standard because its composition lies roughly midway between that of G-1 and W-1...". They quoted a report describing the material as "...a medium-grained tonalite composed of oligoclase, quartz, hornblende and biotite with subordinate chlorite...", "...collected ...by the side of the Great North Road between Iringa and Mbeya, at a point ten miles from Igawa...".

The GSC laboratories contributed a considerable quantity of analytical data in the collaborative program on T-1, but our report apparently arrived too late to be included in the only published compilation (Thomas and Kempe, 1963).

Table 43. NIES pond sediment – information values (originators')

Per cent (dry basis)	Pond Sediment PSJ-1
SiO_2	45.8
TiO_2	1.01
Al_2O_3	20.2
Fe_2O_3T	9.72
MnO	0.093
MgO	?
CaO	1.08
Na_2O	?
K_2O	?
L.O.I.	17.9
P_2O_5	?
F	0.028
S	?
Others	0.08?
Sum	95.9 ? (incomplete)
O/F, etc.	0.1?
Sum (corr.)	95.8 ? (incomplete)
ppm	
Co	29
Cr	70
Cu	220
Hg	1.5
Pb	105
Zn	360

Thomas and Kempe suggested a one-standard-deviation trimmed mean (or "preferred mean") as the best estimated of recommended value. A procedure very much like that (elimination of the 20 per cent of reported values that were farthest removed from the overall mean) was used to provide usable values in all but the most recent (Abbey, 1980) of the earlier papers in this series. Unfortunately, those values resulted in a somewhat high summation and a rather poor iron oxide compatibility –i.e. 5.93 vs 6.03 per cent. In view of the improved summation that resulted when the select laboratories method was applied to NS-1 (the only other "single-sample" program), the values for T-1 were also re-calculated in the same way. The change brought about no improvement in the summation, but there was a highly favourable change in the iron-oxide compatibility, namely, to 5.90 vs 5.91. Usable values for T-1 are given in Table 44.

In connection with the work on T-1, Bowden and Luena (1966) issued a word of warning against the dangers in the indiscriminate use of insufficiently well-established values. The warning was timely because many workers who should have known better had been guilty of just such practices. Unfortunately, examples continue to arise in the literature, despite the caution recommended by Bowden and Luena. See, for example, Chakrabarti et al. (1981, 1982) and Abbey (1982b).

NIM – NATIONAL INSTITUTE FOR METALLURGY (South Africa)[1]

(Contact: T.W. Steele, National Institute for Metallurgy. Private Bag X3015, Randburg 2125, South Africa)

This institution, in collaboration with the South African Bureau of standards, the South African Council for Scientific and Industrial Research and the Geological Survey of South

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[1] After most of the text of this report had been completed, it was learned that the name of the "National Institute for Metallurgy" had been changed to "Council for Mineral Technology", or "MINTEK". It is not known at this writing whether or not the change will affect the designations of NIM reference samples. It was therefore decided to retain the old title of the organization and the designations of the samples in this paper.

Table 44. MRT tonalite – usable values (compiler's)

Per cent (dry basis)	Tonalite T-1
SiO_2	62.70
TiO_2	0.58
Al_2O_3	16.69
Fe_2O_3	2.71
FeO	2.88
MnO	0.10
MgO	1.89
CaO	5.08
Na_2O	4.39
K_2O	1.24
H_2O^+	1.52
CO_2	0.07?
P_2O_5	0.14
F	0.05?
S	0.01?
Others	0.19?
Sum	100.24?
O/F,S,etc.	0.03?
Sum (corr.)	100.21?
Fe_2O_3TR	5.90
Fe_2O_3TC	5.91
ppm	
Ba	660?
Co	13?
Cr	20?
Cu	48?
Ga	20?
Ni	10?
Pb	37?
Rb	32?
Sr	390?
V	96?
Zn	180?
Zr	150?

Africa, has formed the "South African Committee for Certified Reference Materials", which has been conducting one of the most comprehensive programs on geologically- and metallurgically-oriented materials. An outline of that work has been described by Steele (1982) and a detailed catalog is available (South African Committee for Certified Reference Materials, 1979). Announcements concerning new reference materials, produced since the catalog was published, are distributed to interested laboratories as they become available.

Samples available represent a variety of ores, metallurgical process materials and rocks. Of those, only the rocks (and some more recently-produced geochemically-oriented materials) are of interest in this work.

The NIM laboratories have also been responsible for organizing the International Study Group for Geological Reference Materials. An example of the work of that group was published by Steele (1977b).

NIM rocks

A suite of six rocks was announced by Russell et al. (1968). They represented a wide variety of compositions, at least two of which were highly unusual.

NIM-D (also later designated SARM 6, for South African Reference Material, six) is a dunite from the "Critical Zone of the Bushveld Complex in the Transvaal", consisting of olivine and orthopyroxene with minor amounts of clinopyroxene, plagioclase and chromite.

NIM-G (SARM-1) is a granite from the acid phase of the Bushveld Complex.

NIM-L (SARM-3) is a lujavrite "from the foyaite group of the Pilansberg Alkaline Complex in the Transvaal". It was described as "an undersaturated igneous rock which consists of nepheline, sphene, aegerine, magnetite and some feldspar". The sample is of particular interest analytically because of its unusually high contents of zirconium, hafnium, strontium, niobium and chlorine.

NIM-N (SARM-4) is a norite "from the Main Zone of the Bushveld Complex in the Transvaal", consisting of orthopyroxene, plagioclase, magnetite, ilmenite and clinopyroxene, with minor amounts of quartz and alteration products.

NIM-P (SARM-5) is a pyroxenite "from the Critical Zone of the Bushveld Complex in the Transvaal", consisting of orthopyroxene, clinopyroxene and plagioclase with minor amounts of olivine and chromite. Although the amount of chromite is described as minor, the chromium content is much higher than that of all other materials mentioned in this report. The magnesium content is significant in that it fits neatly in the gap between that in such samples as CCRMP-MRG-1, CRPG-BR and GIT-IWG-BE-N on the one hand, and the ultrabasic samples such as ANRT-UB-N, ZGI-SW, USGS-PCC-1 and NIM-D on the other. The alumina content also fills a gap between the low levels in ultrabasics and the 10-20 per cent range commonly found in most other types of rock.

NIM-S (SARM 2) is a syenite "from the Phalaborwa Alkaline Complex in the Transvaal", consisting mainly of potash feldspar with minor amounts of quartz, soda feldspar and alkali-amphiboles. Not surprisingly, the potassium content is the highest of all materials mentioned in this work.

Russell et al. (1972) presented the first compilation of data on the six NIM rocks, including major contributions from the Geological Survey of Canada. They also listed medians, means, standard deviations and coefficients of variation for essentially all of the data, as well as after each step of a two-stage stripping, the first eliminating results beyond three standard deviations of the mean, the second after eliminating results beyond one standard deviation of the mean of the values remaining after the first stripping. It was emphasized that the foregoing computations were intended more to illustrate the variability in the available data than to suggest best values.

Abbey (1973) listed a set of usable values, derived by an early version of the select laboratories method, but pointed out that the unusual compositions of some of the samples necessitated the use of a greater degree of subjectivity than usual, and hence that the derived values were to be regarded with rather limited confidence.

In view of the information in the two preceding paragraphs, it came as a surprise when the South African Committee for Certified Reference Materials (1974) produced an "Announcement" and six "Certificates of Analysis" for these samples. The striking feature of the certificates was that the values listed on them turned out to be those produced by the first stripping stage of Russell et al. (1972), although a letter from National Institute for Metallurgy (1972) had stated specifically that "...many more results are needed before these samples can be regarded as geochemical standard reference material". There was thus a contradiction between the view of the Committee that the samples were "certified", and that of NIM that they were not standard reference materials. It was also difficult to reconcile the fact that some of the values on the certificat were shown as "averages", others as "magnitudes", with the overall designation of "certified". Confusion about the status of the samples at that time was evident from the way they were referred to by several authors in subsequent publications.

There were some examples of questionable iron-oxide compatibilities in the 1974 certificates, but perhaps the most striking case concerned the chromium in NIM-P, which the certificate showed as 3.21 per cent Cr_2O_3. The select laboratories method had yielded a value of 3.62! Examination of the raw data in Russell et al. (1972) revealed that the distribution showed a modal peak at about 3.6, but that the initial stripping had failed to remove two outliers, one at 1.0 and one at 2.0.

Subsequent analytical work in our own laboratories cast some doubt as well on the values derived by the select laboratories method. By that time, it was possible to obtain, through the kindness of T.W. Steele, a computer printout of all available results to the end of 1975, complete with much background information on the analytical methods used. A somewhat refined version of the select laboratories method was then applied to the more comprehensive raw data, and the resulting usable values listed in Abbey (1977b). Those values were, in general, closer to those in the NIM Certificates, but they were free from most of the objections to the latter values. The Cr_2O_3 percentage in NIM-P had come down from 3.62 to 3.53.

Somewhat later, two new reports appeared (Steele et al., 1978; Steele and Hansen, 1979). Included were essentially the raw data in the computer printout mentioned above, a variety of derived statistical measures and subjective choices made from among them to produce recommended, uncertain and magnitude values. The same values appeared in a new set of certificates (South African Bureau of Standards, undated) and in the catalog (South African Committee for Certified Reference Materials, 1979). The NIM estimate of the Cr_2O_3 content of NIM-P had now risen from 3.21 to 3.50 per cent. The gap between the GSC and NIM estimates, originally 3.62 vs 3.21, had shrunk to 3.53 vs 3.50.

In keeping with the policy of favouring values derived by the originators of reference materials, those of Steele et al. (1978) and of Steele and Hansen (1979) were given priority in Abbey (1980), as well as in this work. With few exceptions there were insignificant differences between the originators' values and those of Abbey (1977b).

One exception involved gallium in NIM-L, for which the median of the five available results from select laboratories was 30 ppm, the mean 35 ppm. The latter was listed as a usable value in Abbey (1977b). Steele et al. (1978), after rejecting two extremely high outliers, found a mean of 43 ppm, median 49 ppm and dominant cluster mode 54 ppm. They recommended 54? ppm, a value supported by additional results received after the computations had been completed.

Here we have a case of a rather poor result produced by the select laboratories method. How did that come about? The 15 results originally available were 13, 26, 26, 30, 40, 45, 52, 53, 53, 54, 55.3, 57, 60, 140 and 400 ppm. Only the five underline values were reported by the select laboratories. Clearly, it was poor judgment to accept the five select values as truly representative because they appear to occur in three clusters, each differing from the adjacent one by approximately a factor of two. Under such circumstances, it would have been wiser to accept the median value of all results, which would have yielded a usable value of 53?, quite close to the 54? of Steele and Hansen, and further supported by a moving histogram mode of 54.5. Thus the present author was in this case guilty of what he has accused so many others, namely, blind adherence to a computational procedure where it was evidently not applicable.

Table 45. Comparison of iron oxide values in NIM rocks (pct., dry basis)

Sample	Constituent	Abbey (1977b)	Steele and Hansen (1979)	This work (selected values)
NIM-D	Fe_2O_3	0.90	0.71?	0.71
	FeO	14.46	14.63?	14.63
	Fe_2O_3TR	16.96	17.00	16.96
	Fe_2O_3TC	16.97	16.97?	16.97
	Sum (corr.)	100.22?	100.13?*	100.16?
NIM-G	Fe_2O_3	0.58	0.6?	0.58?
	FeO	1.30	1.30	1.30
	Fe_2O_3TR	2.02	2.00	2.02
	Fe_2O_3TC	2.02	2.04?	2.02?
	Sum (corr.)	99.96?	99.99?	99.99?
NIM-L	Fe_2O_3	8.74	8.78	8.74
	FeO	1.08	1.13	1.13
	Fe_2O_3TR	9.96	9.91	9.96
	Fe_2O_3TC	9.94	10.04	10.00
	Sum (corr.)	99.72?	99.85?	99.87?
NIM-N	Fe_2O_3	0.76	0.8?	0.8?
	FeO	7.30	7.47	7.30
	Fe_2O_3TR	8.91	8.97	8.91
	Fe_2O_3TC	8.87	9.10?	8.91?
	Sum (corr.)	99.80?	100.13?	99.94?
NIM-P	Fe_2O_3	1.02?	0.87?	1.02?
	FeO	10.59?	10.59?	10.59?
	Fe_2O_3TR	12.76	12.70	12.76
	Fe_2O_3TC	12.79?	12.64?	12.79?
	Sum (corr.)	99.77?	99.66?	99.79?
NIM-S	Fe_2O_3	1.07	1.11	1.07
	FeO	0.30	0.30	0.30
	Fe_2O_3TR	1.40	1.40	1.40
	Fe_2O_3TC	1.40	1.44	1.40
	Sum (corr.)	100.17	100.13?	100.16?

* See text

The other discrepancy in results between Steele and Hansen (1979) and Abbey (1977b) concerned the iron oxides. Compatibilities appeared to be better from the latter source, but recognizing that the originators' values should receive some priority, it was decided to compare the two sets of data, item by item, and to select from them those items that, when suitably combined, yielded the best iron-oxide compatibilities and summations. The actual values involved are shown in Table 45. It will be noted that, for five of the six samples, the compatibility of the iron oxides has been improved over, or kept equal to, the better of the two original compatibilities.

In the one case where compatibility was not improved (NIM-L), the difference between the two total iron oxide values is still within acceptable limits, the choice having been based on the desire to improve the summation. The sums shown under Steele and Hansen in Table 45 are not the same as in their original publication because they include allowance for a few more trace elements than were added in by those authors.

Table 46 shows usable values for the six NIM rocks. The large number of elements for which usable values are given should make these samples among the most useful.

Table 46. NIM rocks – usable values (originators', except where shown*)
(Values in parentheses are mere magnitudes, not usable)

Per cent dry basis	Dunite NIM-D	Granite NIM-G	Lujavrite NIM-L	Norite NIM-N	Pyroxenite NIM-P	Syenite NIM-S
SiO_2	38.96	75.70	52.40	52.64	51.10	63.63
TiO_2	0.02	0.09	0.48	0.20	0.20	0.044
Al_2O_3	0.3?	12.08	13.64	16.50	4.18	17.34
Fe_2O_3	0.71	0.58?*	8.74*	0.8?	1.02?*	1.07*
FeO	14.63	1.30	1.13	7.30*	10.59?	0.30
MnO	0.22	0.021	0.77	0.18	0.22	0.01
MgO	43.51	(0.06)	0.28	7.50	25.33	0.46
CaO	0.28	0.78	3.22	11.50	2.66	0.68
Na_2O	0.04?	3.36	8.37	2.46	0.37	0.43
K_2O	0.01?	4.99	5.51	0.25	0.09	15.35
H_2O^+	0.30	0.49	2.31	0.33	0.26	0.22
CO_2	0.40?	0.10?	0.17	0.10?	0.08?	0.09
P_2O_5	0.01?	0.01?	0.06	0.03?	0.02	0.12
F	?	0.42	0.44	(0.01)*	(0.00)*	0.12?*
S	0.02?	0.014?*	0.065?	0.012?*	0.02?*	0.015?*
Others	0.77?	0.19?	2.53?	0.13?	3.67?	0.34?
Sum	100.18?	100.18?	100.11?	99.94?	99.81?	100.22?
O/F,S,etc.	0.02?	0.19?	0.24?	0.01?	0.01?	0.06?
Sum (corr)	100.16?	99.99?	99.87?	99.93?	99.80?	100.16?
Fe_2O_3TR	16.96*	2.02*	9.96*	8.91*	12.76*	1.40
Fe_2O_3TC	16.97	2.02?	10.00	8.91?	12.79?	1.40
ppm						
As		(15)*				
B	(5)*	(7)*				(13)*
Ba	10?	120?	450	100*	46?	2400
Be	(0.5)*	7?*	20?*	1?*		1.4?*
Ce	(9)*	200*	230?	10?*	50?*	11?
Cl	400?*	170?*	1200	100?*	(100)*	(80)*
Co	210*	4?*	8?*	58	110	3?
Cr	2900	12	10?	30?	24000	12
Cs		1?*	4?*			6?*
Cu	10	12	13	14	18	19
Dy		(15)*				(0.6)*
Eu		0.4?*	1?*	0.6?*	0.2?*	0.3?*
Ga		27	54?	16	8?	11
Hf		12?*	190?*			(0.8)*
La		105?*	200?*	3?*	2?*	
Li	4?*	12?	48?	6?*		2?*
Lu		2?*	(0.4)*	(0.2)*		
Mo	(4)*	3?*	4?*	(5)*		
Nb		53	960	(2)*		(4)*
Nd		68?*	45?*			6?*
Ni	2050*	8?	11?*	120	560*	7?
Pb	7?*	40	43	7?*	6?*	5?
Rb		320*	190	6?*	5?*	530
Sb		(0.6)*	(0.3)*	(0.4)*	(0.8)*	(0.6)*
Sc	7?*	1?*	0.3?*	38?*	29?*	4?*
Sm		16?*	(6)*	(0.8)*		(1)*
Sn	2?*	4?*	7?*	(1)*	(2)*	
Sr	3?	10	4600	260	32	62
Ta		4.5?*	22?*			
Tb		3?*	0.7?*			(0.1)*
Th	0.8?*	52	65	(0.6)*	1?*	0.9?
Tm		(2)*				
U		15?	14	0.6?*	0.4?*	0.6?*
V	40	2?	81	220	230	10
Y		145*	25?	6?	6?*	20?*
Yb		14	4?*	0.8?*	(0.6)*	(0.1)*
Zn	90	50	400*	68	100	10?
Zr	(20)*	300	11000	23?	30?	33?

Table 47. NIM kimberlite, shale, soil and dolerite – information values

Per cent	Kimberlite S-7	Carbonaceous shale S-9	"Ni-Cu-Co" soil S-10	Dolerite S-18
SiO_2	32	63.7	70.5	51.9
TiO_2	0.5	0.5	0.4	0.9
Al_2O_3	3	12.6	12.8	15.4
Fe_2O_3T	4	0.8	5.0	11.2
MnO	0.1	0.03	0.1	0.2
MgO	25	10.0	1.6	7.2
CaO	9	1.2	1.0	10.9
Na_2O	0.3	0.03	0.1	2.3
K_2O		1.3	0.4	0.7
L.O.I.		11.0	8.5	0.2
P_2O_5		0.01	0.03	
F				
Others	0.76	0.08	0.92	0.17
Sum	Incomplete	101.25??	101.35??	101.07??
ppm				
Ba				200
Co	60	20	20	42
Cr	3500	120	6000	260
Cu	50	20	1.5	87
Nb				5
Ni	1000	100	130	84
Pb	10	30	30	
Rb	50	40	20	14
Sn	10			
Sr	200	100	20	195
V	220	40	10	230
Y	10	20	15	24
Zn	60	70	1.5	77
Zr	200	150	200	92

Later NIM geological samples

In recent years, NIM undertook to evaluate 14 additional geological reference samples. They were originally analyzed by several South African laboratories, but insufficient data were produced for assigning recommended values. A number of "well chosen overseas laboratories" (including those of GSC) were then invited to contribute to the evaluation.

Frick (undated) described the geological background of 11 of the 14 samples. Of those, two (a carbonatite and a magnesite) were outside the composition ranges included in this work. The remainder were as follows:

S-7 is a kimberlite, obtained from the crushed ore from the De Beers Diamond Mine, Kimberley, Cape Province.

S-9 is a carbonaceous shale from a quarry on the slope of the Engelberg mountain, Marico district, Western Transvaal.

S-10 was described by Frick as a "Co-Cu-Ni rich soil", from the western bank of the Sterkstroom, where it runs parallel to the Marikana-Rustenburg road. Although its source suggested possible enrichment in copper, nickel, cobalt and chromium, preliminary analysis at NIM indicated marked enrichment mainly in chromium.

S-12 is a sillimanite schist from the Swartkoppies mine in the Pofadder district.

Table 48. NIM schists, serpentine and fluorite-rich granite – information values.

Per cent	Sillimanite schist S-12	Garnet schist S-13	Serpentinite S-15	Fluorite-rich Granite S-16
SiO_2	42.8	26.1	37.6	56.9
TiO_2	1.5	5.6	0.05	0.1
Al_2O_3	31.0	66.9	1.8	14.0
Fe_2O_3T	14.6	0.4	4.5	0.2
MnO	0.2	0.01	0.01	0.1
MgO	4.6	0.02	40.0	1.8
CaO	0.6		0.09	13.0
Na_2O	0.1		0.10	3.0
K_2O	0.7	0.1	0.08	4.2
L.O.I.	3.5	0.3	14.7	1.0
P_2O_5	0.4		0.03	0.1
F				4.4
Others	0.26	0.17	0.00	0.16
Sum	100.26	99.60	98.96	98.96
O/F, etc.				1.85
Sum (corr.)				Incomplete
ppm				
Co	10	40	1	
Cr	400	220	0.5	20
Cu	10	10	1	10
Mo	5			
Nb	47		5	
Ni	10	50	3	300
Pb	20	10		120
Rb	73	120	7	180
Sn				1
Sr	10	50	5	38
Th	23		5	120
U				25
V	500	300	15	
Y	33		5	410
Zn	300	80	2	50
Zr	420	300	10	130

S-13 was intended to be a "corundum schist", but examination of the material actually collected suggested "garnet schist" as a more appropriate term. It was collected on a farm west of Augrabies, in the Kankamas district, Orange Free State.

S-14 (as well as S-19 and S-20) was referred to by NIM mainly as "stream sediments", with no indication of their origins. They were not mentioned by Frick.

S-15 is a serpentinite from the M'sauli asbestos mine in the Eastern Transvaal

S-16 is a fluorite-rich granite from the Buffalo fluorspar mine, near Naboomspruit, Northern Transvaal.

S-17 is a "high-purity quartz" from the Silica Smelters, near Pietersburg.

S-18 is a dolerite from a quarry near Jamestown, on the road to Alliwal North.

(Note: The background literature provided with these samples appeared to be of a preliminary nature, including a number of apparent spelling and typographical errors. The reliability of the foregoing information must therefore be taken with some reservation.)

Table 49. NIM quartz and stream sediments – information values

	Quartz	Stream Sediments		
ppm	S-17	S-14	S-19	S-20
TiO_2	1			
Al_2O_3	60			
Fe_2O_3T	5			
MnO	0.2			
MgO	2			
CaO	40			
Na_2O	15			
K_2O	15			
P_2O_5	20			
As		900	100	30
Cr	0.1			
Cu	0.2	500	120	110
Mo		< 10	<10	<10
Ni	0.1	180	170	160
Pb	0.2	11500	1500	500
Rb	0.1			
Sr	1			
Zn	0.6	13000	1500	100

Tables 47, 48, 49 gives information values only for the 12 samples. The groupings into the individual tables are arbitrary, merely to facilitate tabulation. The data clearly indicate that much more analytical work will be needed before these 12 samples can be recognized as useful reference materials. However, their ranges of composition are very interesting, including a number of unusually high concentrations for some "trace" elements, which should eventually prove highly useful in calibration work.

OTHER POTENTIAL REFERENCE MATERIALS

In preparing this paper, efforts were made to achieve comprehensive coverage of as many reference materials as possible. Some samples were included even though they had evidently not yet attained the level of acceptably usable reference materials. Some hitherto unknown to the author came to light while this work was in progress; others may have been overlooked.

Roelandts (1981) attempted an overview of the "weaknesses and strengths" of available rock reference materials, but his work concentrated on the state of knowledge of the contents of specific elements in the various samples. To that end, values were divided into four categories:

(i) "recommended values" (X);
(ii) no recommended value, but 10 or more results reported (A);
(iii) fewer than 10 results reported or fewer than three measurement techniques used (B); and
(iv) no values reported (C)

Comments were offered by Roelandts on well-known sources of error and on the limitations of sensitivity in determining trace elements and others that occasionally occur at much lower levels than usual.

To the extent that Roelandts' work drew attention to the pressing need for redoubled effort in the production and evaluation of reference materials, it was a useful contribution. On the other hand, he did not emphasize the mutual inter-dependence of analytical methodology and the availability of reliable values – i.e. evaluation depends on the use of sensitive and selective methods, but many of those methods require reference materials for calibration purposes. Although he admitted that the various originators of reference materials have used varied approaches to the derivation of recommended values, Roelandts did not mention that what one originator might consider a good value, others might consider only a rough estimate. Further, he confined his study to some 30 samples of the more than 100 available at the time, completely ignoring such major sources as ZGI.

Date (1982) described the problems faced by those who produce and those who use geological reference materials. Of all those who had reviewed the subject, Date came closest to the viewpoints favoured in this paper, perhaps even overstating the case with the words "...the tendency during the second 15-year period [of the history of geological reference samples] has been towards the 'select laboratories' concept as a means of limiting the initial spread of results subjected to statistical analysis". In fact, this writer knows of no other publication in which the "select laboratories" concept has been favoured, although several authors have apparently recognized the need to temper their statistical computations with a degree of subjective judgement (e.g. Govindaraju, 1980, 1982; Steele et al., 1978; Steele and Hansen, 1979).

As might be expected, Date gave major emphasis to his earlier work (Date, 1978) on the production of synthetic reference materials. His scheme involves the preparation of two solutions, one of tetra-ethyl orthosilicate in ethanol, the other a dilute nitric acid solution of such salts of all elements (other than silica) that can be converted to oxides on ignition. The two solutions are combined, and addition of a small amount of ammonium hydroxide results in a "flash hydrolysis", producing a gel in which the dissolved compounds are "frozen" in place. Careful drying and ignition results in the production of a homogeneous powdered mixture of silica and oxides of all other added elements – without the fractional crystallization that would occur if a liquid solution were evaporated.

The major advantage of such a scheme is the ability to vary composition at will. A disadvantage is that the physical characteristics of the product are very different from those of powdered rocks. The powder tends to be light and fluffy, easily subject to electrostatic effects. Individual elements are not likely to occurr in phases corresponding to the mineralogical make-up of a rock. Experiments in our own laboratories have revealed that high ignition temperatures (1200°C?) are necessary to render the product non-hygroscopic, but such treatment can lead to loss of some volatile constituents.

As described by Date (1982), the method can be applied in many cases, but its limitations should not be overlooked.

Ophiolite GOG-1 (Italy)

Benedetti et al. (1977) provided a compilation of data on this ophiolite gabbro, the results of a collaborative effort by five Italian and French institutions. No information was given on the location from which the sample was collected, nor on its geological background. The authors were apparently of the opinion that the material was well on the way to being accepted as a reliable reference sample. However, Harris et al. (1981) pointed out some striking contradictions between the average values reported by Benedetti et al. and the averages of results obtained by several different techniques in USGS laboratories. Any derived values must therefore be regarded as "for information only".

Table 50. Three miscellaneous samples – information values

Per cent (dry basis)	Ophiolite gabbro GOG-1	Purington Shale KnC-ShP-1	Waste incineration ash WIA-1
SiO_2	44.92	60.7	30.18
TiO_2	0.09	0.94	1.18
Al_2O_3	19.38	17.75	15.65
Fe_2O_3T	4.85	7.12	10.87
MnO	0.06	0.10	0.16
MgO	12.61	1.96	2.77
CaO	9.28	0.51	14.10
Na_2O	1.96	1.32	2.22
K_2O	0.05	3.28	4.0
H_2O^+	?	4.52	
CO_2	?		
P_2O_5	0.02	0.14	0.7
F			0.15
Others	0.12	0.16	7.32
Sum	Incomplete	98.50	89.30
O/F, etc.			0.35
Sum (corr.)			Incomplete
ppm			
Ag			42
As			86
Au			0.6
Ba	140	640	4200
Br			140
C (total)			2.5 (pct)
Cd			250
Ce	11		57
Cl			1.28 (pct)
Co	49		35
Cr	75	95	420
Cs	0.2		16
Cu	52	35	750
Eu	0.3		0.2
Ga			260
Ge			16
Hf			3.6
Hg			0.3
I			24
La	0.4		34
Li	2		
Lu			0.6
Mo			24
Nb			16
Nd			44
Ni	470	61	125
Pb		12	6400
Rb		135	140
Sb			220
Sc	3.5		18
Se			22
Sm			6
Sn			3500
Sr	175	125	780
Ta	0.6		1.8
Tb			0.6
Th			11
Tl			82
U			4.2
W			36
Y			34
Yb	0.4		1.6
Zn	24	95	1.2 (pct)
Zr		220	150

Table 50, which also contains values for two other samples, shows median values for GOG-1, based on a combination of the values of Benedetti et al. and those of Harris et al. It is clear that this material has great potential for future use, but much analytical work remains to be done.

Knox College Shale (U.S.A.)

Moore (1978), deploring the shortage of reference samples of argillaceous rocks (and sedimentary rocks in a more general sense), proposed a Purington Shale as a candidate material. The material, designated KnC-Sh P-1 (for Knox College, Shale Purington, one) is from the Liverpool cyclothem in the Carbondale Formation in the Illinois Basin region. More detailed information on the material and its preparation were given by Moore, along with analytical data provided by 10 laboratories, some of which utilized more than one technique. Mean values and standard deviations were calculated for most major and minor constituents, as were also adjusted means and standard deviations for some constituents after deletion of results lying beyond three standard deviations of the overall mean. Reported results for trace elements were relatively few.

Values shown for this material in Table 50 are for information only, being the medians of reported results. The sample shows promise as a badly needed reference material, requiring merely the accumulation of much more analytical data.

BAM incineration ash (West Germany)

The Bundesanstalt für Materialprufung (BAM), of West Berlin, has made a detailed study of a sample of waste incineration ash (herein designated WIA-1), as described by Schmitt et al. (1980). Although intended for use in environmental studies, materials of this nature frequently prove useful in geological work.

Although the work of Schmitt et al. covered a large number of elements, the material cannot yet be regarded as a well-established reference sample. For one thing, all of the reported results were based on either neutron activation or photon activation methods. For another, a relatively small quantity of the material was prepared. Fortunately, the originators reported that a much larger second batch of similar material was being prepared, with the intention of soliciting collaborative analyses by many laboratories, using a variety of techniques. We can therefore look forward to a highly useful reference material.

The information values for WIA-1 in Table 50 are taken entirely from the report by Schmitt et al. (1980), but have been re-cast in the conventional rock analysis layout. Where Schmitt et al. listed more than one value, the median was used in Table 50.

WACOM (Netherlands)

In 1975, this writer was provided with a granite sample powder labelled "WACOM-Gran-1" with the information that it was intended for evaluation as a reference material. The contact person was given as N. Boelrijk, Lab. Isotopen-Geologie, de Boelaan 1085, Amsterdam, The Netherlands. No additional information appears to have been published.

FUB - Federal University of Bahia (Brazil)

In 1976, Prof. Pedro Sampaio Linhares, of the FUB Institute of Geosciences announced two proposed reference rocks, basalt BB-1 (from the Novo Hamburgo region in Rio Grande do Sul) and granite GB-1 (from the Campo Formoso region in Bahia). Again, no further information has been forthcoming.

PART III

THE "CONCENTRATION LADDERS"

GENERAL

Part I of this work described the history and underlying principles of the "study in 'standard samples'". Part II gave background information and concentration values for a large number of available reference materials, most of which are considered suitable for use in rock analysis. Both of those parts are expected to be useful sources of information about the subject and about particular reference samples. But what about the needs of the practicing analyst? In using reference materials, the analyst normally does not approach the task in terms of specific reference materials, but in terms of compositions or concentrations of particular constituents. For example, if one wishes to calibrate an instrument for, say, MgO determination between 0.0 and 10.0 per cent, one seeks out reference samples with MgO contents in that range, observing also the variations in the concentrations of other constituents and paying due attention to possible sources of interference.

In order to facilitate such an approach, the idea of what are herein referred to as "concentration ladders" was introduced in one of the earliest reports in this series (Abbey, 1972). A concentration ladder may be defined as a listing of reference samples in the order of their contents of a specific constituent, as shown in Tables 51 to 118.

Tables 51-67 are concentration ladders for all normally major and minor constituents of the available samples, Tables 68-118 for trace elements. The constituents are presented in the same sequence as in the Tables of Part II. In the tables of Part III, the values listed are those shown as "usable" (with or without question marks) in Tables 9-46. Those shown as "magnitudes" or "information values" in the earlier tables are not included in Tables 51-118 because they are not considered suitable for analytical use. Unfortunately, there may well be some unreliable values among those listed as "usable", not to mention possible errors which are inevitable in handling as voluminous a quantity of data as shown in this paper. Readers are requested to draw the author's attention to any errors, omissions, duplications and other discrepancies.

In Tables 68-118, where a concentration is 50 ppm or higher, the equivalent percentage of the corresponding oxide is also shown, to two decimal places. Exceptions to this rule are carbon, fluorine and chlorine, where the percentage of the element is shown. Where the concentration of a nominally "trace element" is one per cent or higher, the percentage only is shown.

It will be observed that significant figures listed in the concentration ladders (as well as in some earlier tables) differ from those listed by the originators of particular samples in their published reports. In many cases where the originators listed uncertainty limits, it was clear that the last one or two listed significant figures were hardly justifiable.

The general rules followed in this work (as in some others by the present writer) are, firstly, that major and minor constituents are reported to two decimal places in per cent. Exceptions are made where the originators' assigned values go only to the first decimal place, and also, where the first place after the decimal point is a zero (for relatively low concentrations – i.e. under 0.1 per cent) and the originators reported assigned values to a third decimal place.

Secondly, for trace elements, no more than two significant figures should be listed, except where the first digit is unity, where a five is permitted in the third significant place. Exceptions are made in a few special cases where there is good reason to believe that the extra significant figures are justified.

USE OF THE TABLES

The tables in this paper have been designed to provide maximum usefulness to the users of rock reference samples. A possible use of Tables 51-118 has been suggested in the immediately preceding section.

Table 7 is intended for those who wish to restrict their selection of reference samples to one or a few rock types. Having found the designations of the samples of potential usefulness, the user would then refer to the alphabetical listing in Table 8, where the designations are, in some cases, more specific. Table 8 would then refer the reader to the page in the text where the sample is described and where a neighboring table provides compositional information (i.e. Tables 9-30, 32-44, 46-50).

If, on the other hand, an analyst has a particular reference sample or more on hand, their backgrounds and compositions can be obtained by first finding them in the listing in Table 8, which would then lead to the sequence described in the preceding paragraph.

Because of the inevitable occurrence of errors, omissions and other discrepancies in a compilation of so large a quantity of numerical data, readers are urged once more to inform the author of any such occurrences.

Table 51. SiO_2 contents, in descending order (dry basis)

SiO_2 pct	Sample	SiO_2 pct	Sample	SiO_2 pct	Sample	SiO_2 pct	Sample	SiO_2 pct	Sample
99.6	BCS-313	67.5	BCSS-1	60.39	MO8-1	51.10	NIM-P	39.32	MRG-1
99.35	SS	67.32	GSP-1	60.24	TB	49.90	BHVO-1	39.05	SW
95.9	BCS-267	67.1	BCS-375	60.10	SY-2	49.75?	I-3	38.96	NIM-D
88.15?	FK	67.1	BCS-376	59.68	SY-3	49.51	BM	38.42	Mica-Mg
82.92	GSD-8	67.1	NBS-70a	59.66	STM-1	49.2 ?	GXR-1	38.39	BE-N
75.85	GH	67.0 ?	GXR-4	59.61	AGV-1	49.2 ?	GXR-2	38.39	BR
75.70	NIM-G	66.89?	G-B	58.48	GSD-1	49.12	ST-1A	36.50	DT-N
75.36?	I-1	66.74	MA-N	56.44	GSD-5	49.0 ?	GXR-6	35.73	SLg-1
73.50	GM	66.15	SDC-1	55.59?	M-3	48.94	NBS-98a	34.55	Mica-Fe
73.47	RGM-1	66.1	MESS-1	55.02	SO-1	48.88?	M-2	34.4	BCS-367
73.36	SG-1A	65.98	GS-N	54.53	BCR-1	48.8	NBS-1633a	34.1	BCS-309
73.05	NBS-278	65.97	GR	53.46	SO-2	48.4	NBS-688	33.93	SO-3
72.68	G-1	65.93	QLO-1	53.22	NS-1	48.00	BIR-1	33.65	ES-878-1
72.36	JG-1	65.2	NBS-99a	52.98	DR-N	47.29	DNC-1	32.1	IS-1
71.45	GnA	65.11	FK-N	52.81	W-2	47.06	KK	28.30	SGR-1
71.34	GSD-3	64.70	GSD-7	52.72	W-1	46.39	SGD-1A	17.80	ES-681-1
69.96	GA	63.63	NIM-S	52.68	GSD-4	46.35	AN-G	13.4	NBS-69a
69.94	GSD-2	63.39	SCo-1	52.64	NIM-N	43.67	NBS-97a	13.0 ?	GXR-3
69.22	G-2	62.71	TS	52.60?	JB-1	42.10	PCC-1	7.43	BX-N
68.5 ?	SO-4	62.70	T-1	52.40	NIM-L	42.1 ?	GXR-5	6.80	NBS-697
67.53	NBS-91	61.22	GSD-6	52.22	GL-O	40.61	DTS-1	3.80	NBS-696
				51.19?	MAG-1	39.93	UB-N	1.24	BCS-395

Table 52. TiO_2 contents, in descending order (dry basis)

TiO_2 pct	Sample	TiO_2 pct	Sample	TiO_2 pct	Sample	TiO_2 pct	Sample	TiO_2 pct	Sample
3.69	MRG-1	1.21	NBS-1633	0.78	SOIL-5	0.43	GXR-4	0.12	NBS-81a
2.7	NBS-696	1.17	NBS-688	0.75	BCS-367	0.38	BCS-375	0.11	GXR-1
2.69	BHVO-1	1.14	BM	0.75	GSD-7	0.38	GA	0.11	UB-N
2.62	BE-N	1.09	DR-N	0.75	MAG-1	0.35	GXR-5	0.09	NIM-G
2.61	BR	1.07	GSD-3	0.734	BCSS-1	0.35?	G-B	0.08	GH
2.60	I-3	1.07	W-1	0.72	M-2	0.32?	SO-3	0.072	SG-1A
2.6	NBS-697	1.06	AGV-1	0.71	M08-1	0.27	JG-1	0.07 ?	GL-O
2.51	Mica-Fe	1.06	W-2	0.71	TS	0.27	RGM-1	0.059?	FK
2.38	BX-N	1.05	NS-1	0.68	GS-N	0.26	G-1	0.05	I-1
2.26	BCR-1	1.02	IS-1	0.66	GSP-1	0.245	NBS-278	0.044	NIM-S
2.0	NBS-69b	1.00	SDC-1	0.65	GR	0.24	SGR-1	0.036	SS
1.93	BCS-309	0.98	GSD-1	0.62	ES-878-1	0.23	GSD-2	0.023	GnA
1.93	BCS-395	0.96	BIR-1	0.62	QLO-1	0.22	AN-G	0.022	BCS-313
1.90	NBS-97a	0.93	TB	0.62	SCo-1	0.21	GM	0.02	NIM-D
1.82	ST-1A	0.905	MESS-1	0.61	GSD-8	0.20	NIM-N	0.02?	FK-N
1.71	SGD-1A	0.90	GSD-4	0.58	T-1	0.20	NIM-P	0.019	NBS-91
1.64	Mica-Mg	0.90	GSD-5	0.57	SO-4	0.17	BCS-267	0.016	SW
1.61	NBS-98a	0.88	SO-1	0.49	DNC-1	0.17	GXR-3	0.011	NBS-165a
1.43	SO-2	0.86	SdL-1	0.48	ES-681-1	0.166	KK	0.01	MA-N
1.40	DT-N	0.83	GXR-6	0.48	G-2	0.15	SY-3	0.01	NBS-70a
1.34	JB-1	0.83	M-3	0.48	NIM-L	0.14	SY-2	0.01	PCC-1
1.33?	NBS-1633a	0.78	GSD-6	0.47	GXR-2	0.13	STM-1	0.007	NBS-99a

Table 53. Al_2O_3 contents, in descending order (dry basis)

Al_2O_3 pct	Sample
61.1	BCS-309
59.29	DT-N
54.7	NBS-696
54.45	BX-N
52.4	BCS-395
49.3	NBS-69b
45.7	NBS-697
39.3 ?	GXR-5
38.79	NBS-97a
36.77	KK
35.1 ?	GXR-2
33.19	NBS-98a
31.4 ?	GXR-6
29.83	AN-G
23.97?	M-2
23.58	NBS-1633
21.31	NS-1
20.60	TB
20.5	NBS-99a
20.0	BCS-367
19.8	BCS-375
19.58	Mica-Fe
18.64	FK-N
18.44	STM-1
18.39	DNC-1
17.9	NBS-70a
17.72	SO-1
17.7	BCS-376
17.66	MA-N
17.62?	M-3
17.56	DR-N
17.36	NBS-688
17.34	NIM-S
17.19	AGV-1
16.69	T1
16.50	NIM-N
16.46	MAG-1
16.37	QLO-1
16.25?	G-B
16.23	BM
16.15	ES-878-1
15.94	TS
15.75	GSD-2
15.75	SDC-1
15.72	GSD-4
15.54	BIR-1
15.49	W-2
15.47	GSD-5
15.47	SOIL-5
15.40	G-2
15.28	GSP-1
15.25	Mica-Mg
15.24	SO-2
15.02	W-1
14.88	SGD-1A
14.86	GSD-1
14.76	GR
14.71	GS-N
14.7	GnA
14.62	JB-1
14.51	GA
14.23	ST-1A
14.20	JG-1
14.17	GSD-6
14.15	NBS-278
14.05	G-1
14.0	GXR-4
13.92?	I-1
13.85	BHVO-1
13.84	SG-1A
13.80	RGM-1
13.72	BCR-1
13.70	SCo-1
13.64	NIM-L
13.55	GM
13.46	GSD-7
13.07?	I-3
12.51	GH
12.12	SY-2
12.09	GSD-3
12.08	NIM-G
11.83	BCSS-1
11.80	SY-3
11.7 ?	GXR-3
11.03	MESS-1
10.62	ES-681-1
10.32	SO-4
10.25	BR
10.12	BE-N
9.94	MO8-1
9.63	SLg-1
8.50	MRG-1
7.75	GL-O
7.70	GSD-8
7.2	IS-1
6.69?	GXR-1
6.49	SGR-1
6.22?	FK
6.01	NBS-91
5.76	SO-3
4.18	NIM-P
4.0 ?	NBS-1645
2.94	UB-N
0.85	BCS-267
0.73	PCC-1
0.68	SW
0.66	NBS-81a
0.3 ?	NIM-D
0.25	DTS-1
0.249	SS
0.16	BCS-313
0.059	NBS-165a

Table 54. Fe_2O_3 contents, in descending order (dry basis)

Fe_2O_3 pct	Sample
22.98	BX-N
17.61	GL-O
8.74	NIM-L
8.26	MRG-1
6.72?	TS
5.68?	GSD-3
5.61	BR
5.43	UB-N
5.37	BE-N
5.17?	SW
5.09?	I-3
4.75?	GSD-7
4.66	Mica-Fe
4.59?	GSD-1
4.56	AGV-1
4.53?	GSD-5
4.51?	GSD-4
4.26	SCo-1
4.04?	GSD-6
3.92	ST-1A
3.86	SGD-1A
3.71	DR-N
3.48	BCR-1
3.08	MO8-1
2.89?	STM-1
2.74?	BHVO-1
2.71	T-1
2.54?	PCC-1
2.46?	SDC-1
2.44	SY-3
2.36	JB-1
2.31	NS-1
2.31?	M-2
2.28	SY-2
2.06?	BIR-1
1.99?	Mica-Mg
1.93	GS-N
1.86	NBS-688
1.80?	DNC-1
1.70	GnA
1.70	GSP-1
1.70?	G-B
1.65	GR
1.65?	W-2
1.60	BM
1.56?	GSD-8
1.40	W-1
1.36	GA
1.23?	GSD-2
1.07	G-2
1.07	NIM-S
1.02?	DTS-1
1.02?	NIM-P
0.98?	QLO-1
0.91	TB
0.91?	M-3
0.87	AN-G
0.87	G-1
0.8 ?	NIM-N
0.75	GM
0.71	NIM-D
0.68	SG-1A
0.58?	NIM-G
0.55	DT-N
0.53	NBS-278
0.50?	RGM-1
0.41	GH
0.37	JG-1
0.33?	I-1
0.13	MA-N
0.024?	FK-N

Table 55. FeO contents, in descending order (dry basis)

FeO pct	Sample
18.99	Mica-Fe
14.63	NIM-D
10.59?	NIM-P
10.26	ST-1A
10.04?	I-3
8.96	BCR-1
8.73	W-1
8.63	MRG-1
8.55?	BHVO-1
8.36?	W-2
8.35?	BIR-1
7.64	NBS-688
7.34?	DNC-1
7.30	NIM-N
7.28	BM
6.94?	DTS-1
6.86	SGD-1A
6.77	BE-N
6.75?	Mica-Mg
6.60	BR
6.30?	M-2
6.02	JB-1
5.43	TB
5.41	DR-N
5.17?	PCC-1
3.98?	SDC-1
3.80	GnA
3.62	SY-2
3.58	SY-3
3.33?	M-3
2.98?	QLO-1
2.88	T-1
2.71	UB-N
2.38	MO8-1
2.33?	GSD-1
2.32	GSP-1
2.25	GL-O
2.24	AN-G
2.16	GR
2.10?	STM-1
2.03	AGV-1
2.01?	G-B
2.0 ?	SW
1.65	GS-N
1.62	JG-1
1.60	NS-1
1.53?	GSD-6
1.48?	GSD-7
1.44	G-2
1.41	SG-1A
1.36	NBS-278
1.32	GA
1.30	NIM-G
1.24?	RGM-1
1.18?	GSD-4
1.14	GM
1.13	NIM-L
1.10?	GSD-5
0.96	G-1
0.86?	SCo-1
0.84	GH
0.72?	GSD-3
0.66?	TS
0.57?	GSD-2
0.54?	GSD-8
0.31	MA-N
0.30	NIM-S
0.26	BX-N
0.20?	I-1
0.10	DT-N
0.06?	FK-N

Table 56. MnO contents, in descending order (dry basis)

MnO pct	Sample
2.88	GXR-3
1.27	ES-878-1
1.16	BCS-367
0.86?	SLg-1
0.77	NIM-L
0.44	SdL-1
0.35	Mica-Fe
0.35	NBS-697
0.32	SY-2
0.32	SY-3
0.28	ES-681-1
0.28	M-3
0.26	M-2
0.26	Mica-Mg
0.22	DR-N
0.22	I-3
0.22	NIM-D
0.22	NIM-P
0.22	STM-1
0.21	ST-1A
0.20	BE-N
0.20	BR
0.19	IS-1
0.19	SG-1A
0.18	BCR-1
0.18	NIM-N
0.18	NS-1
0.175	BIR-1
0.17	BHVO-1
0.17	MRG-1
0.17	SGD-1A
0.17	W-1
0.167	NBS-688
0.167	W-2
0.166	GnA
0.15	BCS-267
0.15	GSD-5
0.15	JB-1
0.148	DNC-1
0.14	BM
0.132	ASK-1
0.13	GSD-6
0.13	GXR-6
0.12	DTS-1
0.12	GSD-1
0.12	GXR-2
0.12	PCC-1
0.12	SDC-1
0.12	UB-N
0.12?	GXR-1
0.11	G-B
0.11	GSD-4
0.11	SO-1
0.11	SOIL-5
0.11	VS-N
0.101	NBS-1645
0.10	AGV-1
0.10	MAG-1
0.10	T-1
0.09	GA
0.09	GSD-7
0.09	NBS-69b
0.09	QLO-1
0.09	SO-2
0.083	SW
0.08	SO-4
0.07	SO-3
0.066	MESS-1
0.064	NBS-1633
0.06	GR
0.06	JG-1
0.06	MO8-1
0.056	GS-N
0.052	NBS-278
0.052	TB
0.05	BX-N
0.05	GH
0.05	GSD-3
0.05	SCo-1
0.043	GM
0.04	AN-G
0.04	GSD-8
0.04	GSP-1
0.04	MA-N
0.04	RGM-1
0.04	TS
0.036	ASK-2
0.036	GXR-5
0.032	SGR-1
0.030	BCSS-1
0.03	G-1
0.03	G-2
0.03	GSD-2
0.03	I-1
0.03?	BCS-309
0.025?	NBS-1633a
0.021	NIM-G
0.018	GXR-4
0.015	KK
0.01	NIM-S
0.008	DT-N
0.008?	GL-O
0.008?	NBS-91
0.006	BCS-395
0.006?	FK
0.005?	FK-N
0.003	BCS-375
0.003	NBS-696
0.002	BCS-376
0.001?	BCS-313
0.001?	SS

Table 57. MgO contents, in descending order (dry basis)

MgO pct	Sample
49.80	DTS-1
43.51	NIM-D
43.50	PCC-1
38.5	SW
35.66	UB-N
25.33	NIM-P
20.46	Mica-Mg
13.49	MRG-1
13.35	BR
13.22	BE-N
12.27	SLg-1
10.16	DNC-1
9.71	BIR-1
9.55	ES-878-1
8.47?	SO-3
8.4?	NBS-688
7.76	JB-1
7.50	NIM-N
7.46	BM
7.31	BHVO-1
7.1	BCS-367
7.09	SGD-1A
6.63	W-1
6.39	W-2
5.74	ST-1A
4.8 ?	SdL-1
4.58	GL-O
4.57	Mica-Fe
4.57	SGR-1
4.41	DR-N
4.15	GSD-1
4.0	NBS-1645
3.83	SO-1
3.8	IS-1
3.48	BCR-1
3.13	MAG-1
3.08	GSD-7
2.98	GSD-6
2.79	NBS-1633
2.76	SCo-1
2.74	GXR-4
2.70	SY-2
2.67	SY-3
2.5 ?	SOIL-5
2.44	BCSS-1
2.40	GR
2.31	GS-N
2.02	GXR-5
1.94	TB
1.89	T-1
1.80	AN-G
1.77	TS
1.70	SDC-1
1.52	AGV-1
1.48	ES-681-1
1.46	GXR-2
1.44	MESS-1
1.38?	G-B
1.34	MO8-1
1.06	GXR-3
1.04	QLO-1
1.03	GXR-6
1.01	GSD-4
0.97	GSP-1
0.96	GSD-5
0.95	GA
0.93	SO-4
0.90	SO-2
0.76	JG-1
0.755	NBS-1633a
0.75	G-2
0.68	GSD-3
0.64	NS-1
0.46	NIM-S
0.42	NBS-98a
0.38	G-1
0.38	GM
0.35	GXR-1
0.28	M-3
0.28	NIM-L
0.28	RGM-1
0.26	GSD-8
0.26	M-2
0.23?	NBS-278
0.22	I-3
0.21	GSD-2
0.192	KK
0.17	BCS-309
0.17	NBS-697
0.16?	FK
0.15	NBS-97a
0.11	BX-N
0.10	STM-1
0.06	BCS-267
0.054	SG-1A
0.05	BCS-375
0.04	DT-N
0.04	MA-N
0.033	GnA
0.03	BCS-376
0.03	GH
0.03	I-1
0.02	BCS-395
0.02	NBS-99a
0.01	NBS-696
0.01?	FK-N
0.008?	NBS-91
0.007	SS
0.005?	BCS-313

Table 58. CaO contents, in descending order (dry basis)

CaO pct	Sample
37.48	SLg-1
35.65	ES-878-1
32.4	BCS-367
20.7 ?	SO-3
19.7	GXR-3
15.92	AN-G
14.77	MRG-1
13.94	BE-N
13.87	BR
13.33	BIR-1
12.4	IS-1
12.17?	NBS-688
12.01?	M-3
11.52	DNC-1
11.50	NIM-N
11.33	BHVO-1
10.98	W-1
10.97	SGD-1A
10.89	W-2
10.48	NBS-91
10.20	ST-1A
9.35	JB-1
8.70	MO8-1
8.32	SGR-1
8.26	SY-3
8.20	I-3
7.98	SY-2
7.48	GSD-4
7.07	DR-N
6.97	BCR-1
6.56	NBS-1633
6.46	BM
5.30	GSD-5
5.08	T-1
4.94	AGV-1
4.64	GSD-1
4.18?	G-B
4.0 ?	NBS-1645
3.92	ES-681-1
3.85	GSD-6
3.24	QLO-1
3.22	NIM-L
3.1 ?	SOIL-5
2.74	SO-2
2.66	NIM-P
2.64	SCo-1
2.52	SO-1
2.51	GS-N
2.50	GR
2.45	GA
2.17	JG-1
2.14	NBS-99a
2.03	GSP-1
1.96	G-2
1.75	BCS-267
1.75	M-2
1.70	NS-1
1.66	GSD-7
1.55	NBS-1633a
1.55	SO-4
1.39	G-1
1.39	SDC-1
1.38	MAG-1
1.26	GXR-4
1.22	UB-N
1.21	GXR-1
1.15	GXR-2
1.15	RGM-1
1.09?	STM-1
1.05	GXR-5
1.04	GM
0.983	NBS-278
0.98	GL-O
0.89	BCS-375
0.80	I-1
0.78	NIM-G
0.760	BCSS-1
0.69	GH
0.68	NIM-S
0.674	MESS-1
0.61	GnA
0.60	NBS-697
0.59	MA-N
0.55	PCC-1
0.54	BCS-376
0.43	Mica-Fe
0.35?	SdL-1
0.34	BCS-309
0.33	TB
0.31	GSD-2
0.31	NBS-98a
0.28	NIM-D
0.26	GSD-8
0.25	GSD-3
0.236	KK
0.18	SW
0.17	BX-N
0.14	DTS-1
0.14	GXR-6
0.14	SG-1A
0.13	TS
0.12	NBS-69b
0.12 ?	FK
0.11	FK-N
0.11	NBS-70a
0.11	NBS-97a
0.08?	Mica-Mg
0.05	BCS-395
0.04	DT-N
0.030	SS
0.02	BCS-313
0.01	NBS-696

Table 59. Na_2O contents, in descending order (dry basis)

Na_2O pct	Sample
10.4	BCS-375
9.85	NS-1
8.95	STM-1
8.48	NBS-91
8.37	NIM-L
6.2	NBS-99a
5.85	MA-N
5.46	SG-1A
4.84	NBS-278
4.64	BM
4.59	I-1
4.39	T-1
4.34	SY-2
4.32	AGV-1
4.23	QLO-1
4.15	SY-3
4.12	RGM-1
4.06	G-2
3.91	MAG-1
3.85	GH
3.80	GR
3.78	GS-N
3.76	GM
3.65?	G-B
3.55	GA
3.49	GSD-1
3.39	JG-1
3.36	NIM-G
3.32	G-1
3.30	BCR-1
3.20	BE-N
3.10	GSD-2
3.07	BR
3.02	SGR-1
3.00	DR-N
2.98	M-3
2.92	I-3
2.83	BCS-376
2.82	SGD-1A
2.81	GSP-1
2.79	JB-1
2.72	BCSS-1
2.59	SOIL-5
2.58	FK-N
2.56?	SO-1
2.55	NBS-70a
2.50	MESS-1
2.49	ST-1A
2.46	NIM-N
2.35?	SO-2
2.32	GSD-6
2.29	BHVO-1
2.21	W-2
2.15	NBS-688
2.15	W-1
2.10	SDC-1
1.89	DNC-1
1.82	BIR-1
1.63	AN-G
1.40	M-2
1.31	TB
1.31?	SO-4
1.23	GSD-7
1.05	GXR-3
1.04	GXR-5
1.00	SO-3
0.95	SCo-1
0.78	IS-1
0.75	GXR-2
0.74?	NBS-1645
0.71	GXR-4
0.71	MRG-1
0.50	GSD-8
0.5 ?	MO8-1
0.47	ES-878-1
0.44	BCS-367
0.43	NIM-S
0.42	NBS-1633
0.41	GSD-5
0.39?	SLg-1
0.37	NIM-P
0.34	BCS-309
0.32	GSD-3
0.30	Mica-Fe
0.29	GSD-4
0.25?	FK
0.23	1633a
0.23	SdL-1
0.14	GXR-6
0.12?	Mica-Mg
0.10	UB-N
0.092	ES-681-1
0.09	TS
0.082	NBS-98a
0.08	GnA
0.074	GXR-1
0.06	BCS-267
0.046	NBS-697
0.043	SS
0.04	BX-N
0.04	DT-N
0.04?	GL-O
0.04?	NIM-D
0.037	NBS-97a
0.032	KK
0.03	NBS-69b
0.03?	BCS-395
0.02	NBS-696
0.013	SW
0.01	PCC-1
0.01?	DTS-1
0.008?	BCS-313

Table 60. K_2O contents, in descending order (dry basis)

K_2O pct	Sample
15.35	NIM-S
12.83	FK-N
11.8	NBS-70a
11.2	BCS-376
10.03	Mica-Mg
8.79	Mica-Mg
8.16	GL-O
7.90	M-2
6.52	NS-1
5.51	GSP-1
5.51	NIM-L
5.48	G-1
5.2	GXR-4
5.2	NBS-99a
5.18	GSD-2
4.99	NIM-G
4.88	TS
4.76	GH
4.74	GM
4.64	GS-N
4.50	GR
4.48	SY-2
4.46	G-2
4.35	RGM-1
4.29	STM-1
4.28	I-1
4.20	SY-3
4.16	NBS-278
4.15?	FK
4.14	SG-1A
4.03	GA
3.96	JG-1
3.85	TB
3.72	MAG-1
3.63	QLO-1
3.49	GSD-7
3.25	NBS-91
3.24	SDC-1
3.23	SO-1
3.19	MA-N
2.96	SGD-1A
2.95	SO-2
2.92	AGV-1
2.90?	G-B
2.82	SCo-1
2.78	GSD-1
2.75	GSD-8
2.63	GnA
2.46	GXR-6
2.44	GSD-3
2.43	GSD-6
2.26	NBS-1633a
2.24	MESS-1
2.24	SOIL-5
2.2 ?	MO8-1
2.17	BCSS-1
2.16	GSD-4
2.08	SO-4
2.04	GSD-5
2.00	NBS-1633
1.8 ?	SdL-1
1.70	BCR-1
1.70	DR-N
1.70	GXR-2
1.63	SGR-1
1.43	I-3
1.42	JB-1
1.41	BR
1.40	BE-N
1.4	IS-1
1.40	SO-3
1.4 ?	NBS-1645
1.29	ES-878-1
1.24	T-1
1.17	BCS-367
1.06	KK
1.04	NBS-98a
0.99	GXR-5
0.89?	GXR-3
0.80	NBS-69b
0.78	BCS-375
0.71	M-3
0.69	ST-1A
0.64	W-1
0.63	W-2
0.59	ES-681-1
0.54	BHVO-1
0.51?	SLg-1
0.50	97a
0.46	BCS-309
0.25	NIM-N
0.23	DNC-1
0.20	BM
0.187	NBS-688
0.18	MRG-1
0.14	BCS-267
0.13	AN-G
0.12	DT-N
0.09	NIM-P
0.07	NBS-697
0.064	GXR-1
0.057	SS
0.05	BX-N
0.04	BCS-313
0.03	BIR-1
0.02	UB-N
0.02?	BCS-395
0.014?	SW
0.01	NBS-696

Table 61. H_2O^+ contents, in descending order (dry basis)

H_2O^+ pct	Sample
13.6	SW
12.75	KK
11.53	BX-N
10.98	UB-N
10.4 ?	ES-681-1
5.8 ?	MAG-1
5.72	GL-O
4.70	PCC-1
4.03	TS
3.90?	SCo-1
3.82	TB
3.62	BM
3.21?	M-2
3.0 ?	MO8-1
2.92?	Mica-Fe
2.31	BR
2.31	NIM-L
2.26	DR-N
2.25	BE-N
2.10?	Mica-Mg
1.8 ?	GnA
1.71?	I-3
1.70?	SDC-1
1.52	T-1
1.44?	STM-1
1.08	MA-N
1.07	GS-N
1.01	JB-1
0.98	MRG-1
0.97	ST-1A
0.90	DT-N
0.87	GA
0.83	SGD-1A
0.78	AGV-1
0.78?	M-3
0.73?	DNC-1
0.70	GR
0.67	BCR-1
0.66	NS-1
0.61	AN-G
0.58	GSP-1
0.55?	W-2
0.54	JG-1
0.53	W-1
0.50	G-2
0.50?	RGM-1
0.49	NIM-G
0.46	GH
0.43	SY-2
0.42	DTS-1
0.42	SY-3
0.41?	FK
0.36?	G-B
0.35	GM
0.34	G-1
0.34?	QLO-1
0.33	NIM-N
0.32?	FK-N
0.30	NIM-D
0.26	NIM-P
0.22	NIM-S
0.21	SG-1A
0.20?	BHVO-1
0.13?	I-1
0.016?	BIR-1

Table 62. CO_2 contents, in descending order (dry basis)

CO_2 pct	Sample
5.4 ?	ES-681-1
2.98?	M-3
2.75?	SCo-1
1.34	BM
1.00	MRG-1
0.86	BR
0.74	BE-N
0.46	SY-2
0.44	BX-N
0.40?	NIM-D
0.39	UB-N
0.38	SY-3
0.29?	SW
0.28	GM
0.26	GR
0.19?	Mica-Fe
0.18	PCC-1
0.18?	GS-N
0.18?	JB-1
0.17	KK
0.17	NIM-L
0.15?	Mica Mg
0.14	GH
0.14?	NS-1
0.13	AN-G
0.13	MA-N
0.13	SGD-1A
0.13	TB
0.12	GSP-1
0.11	GA
0.10	DR-N
0.10?	NIM-G
0.10?	NIM-N
0.099	ST-1A
0.09	NIM-S
0.09?	SDC-1
0.085?	FK-N
0.08?	G-2
0.08?	JG-1
0.08?	NIM-P
0.07	DTS-1
0.07	G-1
0.07?	SG-1A
0.07?	T-1
0.06	W-1
0.05?	NBS-688
0.04?	BHVO-1
0.04?	TS
0.025?	FK
0.02	AGV-1
0.02	BCR-1
0.02?	STM-1
0.01?	NBS-278
0.01?	QLO-1
0.01?	RGM-1

Table 63. P_2O_5 contents, in descending order (dry basis)

P_2O_5 pct	Sample	P_2O_5 pct	Sample	P_2O_5 pct	Sample	P_2O_5 pct	Sample	P_2O_5 pct	Sample
11.5	IS-1	0.34	GSD-1	0.18?	MAG-1	0.12?	NBS-1645	0.036	NBS-278
2.02	ES-681-1	0.29	TS	0.16	STM-1	0.11	GSD-4	0.034?	ES-878-1
1.39	MA-N	0.29?	SGR-1	0.154	BCSS-1	0.11	NBS-98a	0.03	GSD-8
1.06	BE-N	0.28	BHVO-1	0.146	MESS-1	0.11?	SO-3	0.03?	NIM-N
1.05	BR	0.28	GR	0.14	GSD-3	0.105	BM	0.026?	SW
1.01	SGD-1A	0.28	GS-N	0.14	GSD-5	0.095	TB	0.024?	FK-N
0.90	NBS-697	0.28	GSP-1	0.14	SO-1	0.09	DT-N	0.022	NBS-91
0.69?	SO-2	0.28	NS-1	0.14	T-1	0.09	G-1	0.021?	BIR-1
0.54	SY-3	0.26	JB-1	0.14	W-1	0.09	JG-1	0.02	NBS-99a
0.51	AGV-1	0.26	QLO-1	0.14	W-2	0.09	KK	0.02	NIM-P
0.50?	M-2	0.25	DR-N	0.14?	BCS-367	0.075?	FK	0.02?	I-1
0.45	Mica-Fe	0.25?	SOIL-5	0.14?	G-B	0.07?	DNC-1	0.016?	GnA
0.43	SY-2	0.23	GSD-6	0.134	NBS-688	0.063	GM	0.013	SG-1A
0.40?	I-3	0.22?	SCo-1	0.13	BX-N	0.06	MRG-1	0.01	AN-G
0.38	GL-O	0.21	SO-4	0.13	G-2	0.06	NBS-696	0.01	GH
0.36	BCR-1	0.21	ST-1A	0.12	GA	0.06	NIM-L	0.01	PCC-1
0.36	NBS-97a	0.19	GSD-7	0.12	MO8-1	0.05?	RGM-1	0.01?	Mica-Mg
0.36?	M-3	0.18	SDC-1	0.12	NBS-69b	0.04	GSD-2	0.01?	NIM-D
				0.12	NIM-S	0.04	UB-N	0.01?	NIM-G

Table 64. F contents, in descending order (dry basis)

F pct	Sample	F pct	Sample	F pct	Sample	F pct	Sample	F pct	Sample
5.72	NBS-91	0.20	GSD-2	0.091?	STM-1	0.06	GSD-5	0.032?	ST-1A
3.36	GnA	0.19	ES-681-1	0.09	GSD-1	0.06?	M-3	0.03	GSD-3
2.85?	Mica-Mg	0.19?	SGR-1	0.09	GSD-7	0.05	BCR-1	0.03?	SO-3
1.70	MA-N	0.15	ES-878-1	0.09?	MAG-1	0.05	GA	0.03?	SO-4
1.58	Mica-Fe	0.15?	GL-O	0.077?	SCo-1	0.05?	NBS-278	0.028?	QLO-1
0.66	SY-3	0.14	NS-1	0.071?	TB	0.05?	SO-2	0.026?	BM
0.51	SY-2	0.12	G-2	0.07	GSD-4	0.05?	T-1	0.025	MRG-1
0.44	NIM-L	0.12	SGD-1A	0.07	GSD-6	0.049?	JG-1	0.025	W-1
0.42	NIM-G	0.12?	NIM-S	0.07?	I-3	0.047?	DR-N	0.02	GSD-8
0.37	GSP-1	0.10	BR	0.07?	SO-1	0.04	AGV-1	0.02?	NBS-688
0.35	GH	0.10	GR	0.069	G-1	0.039?	JB-1	0.014	MO8-1
0.30	SG-1A	0.10?	BE-N	0.067?	GM	0.038?	BHVO-1	0.012?	AN-G
		0.10?	M-2	0.062?	SDC-1	0.034?	RGM-1	0.01?	GS-N

Table 65. S contents, in descending order (dry basis)

S pct	Sample	S pct	Sample	S pct	Sample	S pct	Sample	S pct	Sample
1.56?	SGR-1	0.20?	NBS-91	0.04?	BR	0.02?	SO-3	0.01?	GR
1.26	SLg-1	0.103	ES-681-1	0.04?	SO-4	0.019	KK	0.01?	GS-N
1.2 ?	SdL-1	0.096	NBS-696	0.03?	BE-N	0.017	SG-1A	0.01?	MA-N
0.94	BCS-367	0.068	ST-1A	0.03?	GSP-1	0.015?	NIM-S	0.01?	Mica-Fe
0.81	ES-878-1	0.067?	SDC-1	0.03?	SO-2	0.014?	AN-G	0.01?	NS-1
0.72	IS-1	0.066?	SCo-1	0.022?	TS	0.014?	NIM-G	0.01?	PCC-1
0.72	MESS-1	0.065?	NIM-L	0.02	SGD-1A	0.012?	NIM-N	0.01?	RGM-1
0.46?	MO8-1	0.06	MRG-1	0.02?	GA	0.011	SY-2	0.01?	SO-1
0.43?	MAG-1	0.06	NBS-697	0.02?	Mica-Mg	0.011?	BHVO-1	0.01?	T-1
0.36	BCSS-1	0.05	SY-3	0.02?	NIM-D	0.01?	AGV-1	0.006?	NBS-1633
0.25	NBS-69b	0.04?	BCR-1	0.02?	NIM-P	0.01?	G-2	0.005?	I-1
								0.004?	QLO-1

Table 66. SO_3 contents, in descending order (dry basis)

SO_3 pct	Sample	SO_3 pct	Sample
1.8	IS-1	0.32	BCS-367
0.63	NBS-69b	0.24	NBS-696
		0.15	NBS-697

Table 67. Fe_2O_3T contents, in descending order (dry basis)

Fe_2O_3T pct	Sample	Fe_2O_3T pct	Sample	Fe_2O_3T pct	Sample	Fe_2O_3T pct	Sample	Fe_2O_3T pct	Sample
47.48	ES-681-1	11.11	W-1	7.1	NBS-69b	4.29	QLO-1	1.40	NIM-S
35.3 ?	GXR-1	10.86	W-2	6.98	MAG-1	4.25?	GXR-4	1.36	GH
26.6 ?	GXR-3	10.35	NBS-688	6.92	TB	4.10	NS-1	1.34	NBS-98a
25.76	Mica-Fe	10.00	DNC-1	6.85	SDC-1	4.04	GR	1.11	BCS-367
23.27	BX-N	9.96	NIM-L	6.78	AGV-1	3.89?	G-B	1.02	SLg-1
20.11	GL-O	9.72	DR-N	6.53	GSD-3	3.76	GS-N	0.98	KK
20.0	NBS-697	9.68	BM	6.50	GSD-7	3.39	SO-4	0.86	ES-878-1
18.6	IS-1	9.64	SdL-1	6.42	SY-3	3.36	AN-G	0.79	BCS-267
17.82	MRG-1	9.49?	Mica-Mg	6.36	SOIL-5	2.98	SGR-1	0.66	DT-N
16.96	NIM-D	9.25	M-2	6.28	SY-2	2.77	GA	0.54	I-1
16.3	BCS-395	9.01	JB-1	5.92	GnA	2.7	GXR-2	0.47	MA-N
16.22?	I-3	8.91	NBS-1633	5.90	GSD-4	2.69	G-2	0.45	NBS-97a
16.2	NBS-1645	8.91	NIM-N	5.90	T-1	2.25	SG-1A	0.26?	FK
15.32	ST-1A	8.70	DTS-1	5.85	GSD-6	2.20	GSD-8	0.12	BCS-375
13.41	BCR-1	8.7	NBS-696	5.83	GSD-5	2.16	JG-1	0.10	BCS-376
13.4	NBS-1633a	8.57	SO-1	5.72	MO8-1	2.16	SO-3	0.09?	FK-N
12.90	BE-N	8.45	UB-N	5.22	SCo-1	2.04	NBS-278	0.082	NBS-81a
12.90	BR	8.28	PCC-1	5.20	STM-1	2.02	GM	0.081	NBS-91
12.76	NIM-P	7.98?	GXR-6	4.70	BCSS-1	2.02	NIM-G	0.075	NBS-70a
12.23	BHVO-1	7.95	SO-2	4.56	GXR-5	1.94	G-1	0.065	NBS-99a
11.48	SGD-1A	7.45	TS	4.55	M-3	1.90	GSD-2	0.038	SS
11.30	BIR-1	7.40?	SW	4.36	MESS-1	1.89	RGM-1	0.030	BCS-313
		7.34	GSD-1	4.30	GSP-1	1.53	BCS-309	0.012	NBS-165a

Table 68. Ag contents, in descending order

Ag ppm	Sample	Ag ppm	Sample	Ag ppm	Sample	Ag ppm	Sample	Ag ppm	Sample
2	MA-N	0.4	ASK-2	0.094?	AGV-1	0.07	GSD-2	0.05?	GSD-1
2 ?	SOIL-5	0.37	GSD-5	0.085	GSD-4	0.064	GSD-8	0.05?	JG-1
1.1	GSD-7	0.35	GSD-6	0.083?	GSP-1	0.06?	JB-1	0.04?	G-2
0.59	GSD-3	0.14?	MRG-1	0.081	W-1	0.056?	BHVO-1	0.034?	BCR-1
0.5?	SDC-1	0.1 ?	RGM-1	0.08?	STM-1	0.05	ASK-1	0.01?	DTS-1
								0.01?	PCC-1

Table 69. As contents, in descending order.

As ppm	Sample	*As_2O_3T pct
4000	GXR-3	0.53
1350	NBS-91	0.18
460	GXR-1	0.06
340	GXR-6	0.04
145	NBS-1633a	0.02
120?	BX-N	0.02
100?	ES-681-1	0.01
98	GXR-4	0.01
94	SOIL-5	0.01
83	GSD-7	0.01
74	GSD-5	0.01
66?	NBS-1645	0.01
63?	SGR-1	0.01
61	NBS-1633	0.01
40	IS-1	0.01
31	GXR-2	
30?	MO8-1	
28	SdL-1	
20	SY-3	
19.5	GSD-4	
18	SY-2	
17.5	GSD-3	
15?	SCo-1	
14?	BM	
13.5	GSD-6	
13?	MA-N	
12	GXR-5	
12?	UB-N	
11	BCSS-1	
11	MESS-1	
11?	TB	
6.4	GSD-2	
4?	GM	
3?	DR-N	
2.5	GSD-8	
2.0	GSD-1	
1.9	W-1	
1.2?	W-2	
0.8?	BCR-1	
0.7	MRG-1	

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* Total arsenic, expressed as As_2O_3

Table 70. Au contents, in descending order

Au ppb	Sample
10 ?	SdL-1
4 ?	G-1
3.7?	W-1
1 ?	G-2
1 ?	GSP-1
0.8	BCR-1
0.8?	DTS-1
0.7?	PCC-1
0.6?	AGV-1

Table 71. B contents, in descending order

B ppm	Sample	B_2O_3 pct
300?	VS-N	0.10
180	GXR-3	0.06
155	ASK-2	0.05
145?	UB-N	0.05
130?	MAG-1	0.04
110	SY-3	0.04
92?	TB	0.03
85?	SY-2	0.03
85?	TS	0.03
66?	SCo-1	0.02
50?	SGR-1	0.02
44	GXR-2	0.01
37?	QLO-1	0.01
31?	RGM-1	0.01
25	GXR-5	0.01
25?	NBS-278	0.01
22?	SO-3	0.01
20	GA	0.01
20?	GnA	0.01
17?	MA-N	0.01
16	SGD-1A	0.01
15.3	GXR-1	
15	ST-1A	
14?	GM	
13?	MRG-1	
12?	JB-1	
11	GXR-6	
10	SG-1A	
10?	BR	
6?	AGV-1	
6?	GR	
6?	JG-1	
4.3	GXR-4	
4	BCR-1	

Table 72. Ba contents, in descending order

Ba ppm	Sample	BaO pct
4700	GXR-3	0.52
4000	Mica-Mg	0.45
2600	NBS-1633	0.29
2400	NIM-S	0.27
2300	NBS-99a	0.26
2000	GXR-2	0.22
1950?	TS	0.22
1900	G-2	0.21
1900	IS-1	0.21
1800	GXR-5	0.20
1550?	M-2	0.17
1500?	NBS-1633a	0.17
1400	GS-N	0.16
1400	QLO-1	0.16
1350	GXR-4	0.15
1300	GSP-1	0.15
1300	SGD-1A	0.15
1200	AGV-1	0.13
1200	NS-1	0.13
1150	ASK-1	0.13
1150?	NBS-278	0.13
1100	GXR-6	0.12
1050	BE-N	0.12
1050	BR	0.12
1050	GR	0.12
1000	VS-N	0.11
1000?	SO-2	0.11
950	GSD-1	0.10
900?	SO-1	0.10
850	GA	0.09
800	RGM-1	0.09
780?	SO-4	0.09
730	GSD-7	0.08
720	TB	0.08
690?	I-3	0.08
680	BCR-1	0.08
670	NBS-97a	0.07
660?	T-1	0.07
650	SDC-1	0.07
640	SdL-1	0.07
620	GSD-3	0.07
590	SCo-1	0.07
560	GXR-1	0.06
560	SOIL-5	0.06
560	STM-1	0.06
490	GSD-8	0.05
490	JB-1	0.05
480	MAG-1	0.05
480?	I-1	0.05
460	JG-1	0.05
460	SY-2	0.05
450	GSD-4	0.05
450	NIM-L	0.05
450?	BCS-376	0.05
440	GSD-5	0.05
430	SY-3	0.05
390	DR-N	0.04
330	GM	0.04
330	GSD-6	0.04
300?	NBS-98a	0.03
290	SGR-1	0.03
290	ST-1A	0.03
280?	SO-3	0.03
260	BM	0.03
210?	FK-N	0.02
200?	NBS-688	0.02
190	GSD-2	0.02
180?	NBS-70a	0.02
175	W-2	0.02
160	W-1	0.02
145	Mica-Fe	0.02
135	BHVO-1	0.02
130?	DT-N	0.01
125?	M-3	0.01
120	DNC-1	0.01
120?	NIM-G	0.01
100	NIM-N	0.01
90?	BCS-375	0.01
80?	NBS-697	0.01
50?	MAG-1	0.01
46?	NIM-P	0.01
45?	NBS-696	0.01
42	MA-N	
34	AN-G	
34?	BX-N	
30?	UB-N	
22	GH	
19	SG-1A	
10?	NIM-D	
6.1?	BIR-1	
5?	DTS-1	
4?	PCC-1	

Table 73. Be contents, in descending order

Be ppm	Sample	BeO pct
280	MA-N	0.08
26	GXR-3	0.01
23	SY-2	0.01
22	SY-3	0.01
20?	NIM-L	0.01
17	GSD-2	
12?	KK	
12?	NBS-1633	
12?	NBS-1633a	
11	SG-1A	
9?	STM-1	
8?	Mica-Fe	
7?	NIM-G	
6?	GH	
6?	NS-1	
5.5	GR	
5.5?	BX-N	
5?	GnA	
4	ASK-1	
4	ASK-2	
4?	GM	
4?	TB	
3.6	GA	
3.5?	TS	
3.0	GSD-1	
3?	MAG-1	
3?	SDC-1	
2.7	GSD-7	
2.5?	RGM-1	
2.4	G-2	
2.4	GSD-5	
2.3	GSD-4	
2.1	GXR-4	
2.0	GSD-8	
2	SGD-1A	
2?	AGV-1	
2?	QLO-1	
2?	SOIL-5	
1.9	MESS-1	
1.8?	DR-N	
1.7?	SCo-1	
1.65	GXR-2	
1.6	GSD-6	
1.6?	BCR-1	
1.5	GSD-3	
1.4?	NIM-S	
1.3	BCSS-1	
1.20	GXR-5	
1.2?	BM	
1.10	GXR-1	
1.1	GXR-6	
1	ST-1A	
1?	BR	
1?	GSP-1	
1?	NIM-N	
0.95?	DNC-1	

Table 74. Bi and Br contents, in descending order

Bi ppm	Sample	Bi ppm	Sample	Bi_2O_3 pct	Br ppm	Sample
0.3?	RGM-1	1000?	VS-N	0.11?	11	NBS-1633
0.20	GSD-8	220?	GnA	0.02	7.8	GXR-5
0.065?	G-1	12?	SOIL-5		7	SdL-1
0.05 ?	AGV-1	5.0	GSD-6		5	SOIL-5
0.047 ?	BCR-1	2.4	GSD-5		3.0	GXR-2
0.046?	W-1	1.6	GSD-2		1.4	GXR-6
0.043	G-2	0.81	GSD-3		0.50	GXR-4
0.037	GSP-1	0.68	GSD-7		0.39	GXR-1
0.014?	BHVO-1	0.67	GSD-4		0.2 ?	BCR-1
0.013	PCC-1	0.66	GSD-1			
0.01	DTS-1					

Table 75. C (Non-carbonate), C (Total), and Cd contents, in descending order

C (Non-carbonate) pct	Sample	C (Total) pct	Sample	Cd ppm	Sample
2.2 ?	MAG-1	6.6 ?	SO-3	900 ?	VS-N
1.39	TS	4.8 ?	SO-2	10.2	NBS-1645
0.62	DT-N	4.4 ?	SO-4	9	IS-1
0.33 ?	ES-681-1	2.99	MESS-1	2.8 ?	SS
0.24 ?	SCo-1	2.19	BCSS-1	2?	MA-N
0.047?	NBS-278	2.0	MO8-1	1.5 ?	SOIL-5
0.042?	SG-1A	1.80	ES-681-1	1.45	NBS-1633
0.036	ST-1A	1.40?	TS	1.0	GSD-7
0.028	SGD-1A	0.99?	SCo-1	1.0	NBS-1633a
0.027?	SY-2	0.30?	MRG-1	0.82	GSD-5
0.025?	MRG-1	0.25?	SO-1	0.59	MESS-1
0.025?	SY-3	0.15?	SY-2	0.42	GSD-6
		0.13?	SY-3	0.42?	SO-4
		0.06	ST-1A	0.26	SdL-1
		0.06?	SG-1A	0.25	BCSS-1
		0.06?	SGD-1A	0.2 ?	MAG-1
		0.05?	NBS-278	0.19	GSD-4
				0.18?	SO-2
				0.15	W-1
				0.15?	SO-1
				0.14?	SO-3
				0.10	GSD-3
				0.09?	BCR-1
				0.09?	DR-N
				0.08	GSD-1
				0.079	GSD-8
				0.06	GSD-2
				0.039?	G-2

Table 76. Ce contents in descending order

Ce ppm	Sample	CeO_2 pct
2200	SY-3	0.27
500?	BX-N	0.06
370?	Mica-Fe	0.05
360	GSP-1	0.04
260	STM-1	0.03
230?	NIM-L	0.03
210?	SY-2	0.03
200	NIM-G	0.02
185?	NS-1	0.02
180?	NBS-1633a	0.02
160	G-2	0.02
150	BE-N	0.02
150	NBS-1633	0.02
150	SGD-1A	0.02
140	BR	0.02
125?	DT-N	0.02
115	GXR-4	0.01
115	SdL-1	0.01
115?	TB	0.01
92	SDC-1	0.01
86?	MAG-1	0.01
71	AGV-1	0.01
70	GA	0.01
67?	JB-1	0.01
67?	SG-1A	0.01
63	SCo-1	0.01
62?	NBS-278	0.01
60	SOIL-5	0.01
60?	GM	0.01
59?	QLO-1	0.01
53	BCR-1	0.01
50	GXR-2	0.01
50?	GH	0.01
50?	NIM-P	0.01
48?	RGM-1	0.01
46	DR-N	0.01
45?	G-B	0.01
43?	JG-1	0.01
40	GXR-5	
39	BHVO-1	
38	GXR-6	
38?	SGR-1	
27?	BM	
25?	MRG-1	
23	W-2	
22?	ST-1A	
19	GXR-1	
16	GXR-3	
13?	NBS-688	
11?	NIM-S	
10?	MA-N	
10?	NIM-N	
9.1?	DNC-1	
4.7	AN-G	
1.6?	BIR-1	

Table 77. Cl contents, in descending order

Cl pct	Sample
3.09?	MAG-1
1.12	BCSS-1
0.82	MESS-1
0.12	NIM-L
0.080?	Mica-Mg
0.080?	UB-N
0.054	RGM-1
0.050?	Mica-Fe
0.050?	NS-1
0.045?	STM-1
0.043?	ST-1A
0.040?	DR-N
0.040?	NIM-D
0.037?	BR
0.034	GSP-1
0.030?	AN-G
0.030?	BE-N
0.030?	GA
0.022?	QLO-1
0.022?	SGD-1A
0.0185	AGV-1
0.0175?	JB-1
0.017?	NIM-G
0.015?	MRG-1
0.014?	MA-N
0.014?	SY-3
0.013?	SY-2
0.010	ASK-1
0.010	G-2
0.010?	GH
0.010?	NIM-N
0.0094?	BHVO-1
0.0080?	PCC-1
0.0059?	JG-1
0.0058?	BCR-1
0.0051?	SCo-1
0.0050?	SGR-1
0.0040?	NBS-1633
0.0035?	SDC-1
0.0014	ASK-2
0.0011?	DTS-1

Table 78. Co contents, in descending order

Co ppm	Sample	CoO pct
700	VS-N	0.09
210	NIM-D	0.03
135	DTS-1	0.02
110	NIM-P	0.01
110	PCC-1	0.01
110	UB-N	0.01
100	SW	0.01
86	MRG-1	0.01
65	GS-N	0.01
61	BE-N	0.01
58	NIM-N	0.01
57	DNC-1	0.01
52	BIR-1	0.01
50	BR	0.01
50?	NBS-688	0.01
49?	I-3	0.01
48	GXR-3	0.01
47?	W-1	0.01
46	ST-1A	0.01
46?	NBS-1633a	0.01
45	BHVO-1	0.01
43	W-2	0.01
40	NBS-1633	0.01
40	SGD-1A	0.01
39	JB-1	
38	TS	
36	BCR-1	
35	DR-N	
35?	BX-N	
34	BM	
33?	SO-1	
30	GXR-5	
30?	M-2	
27	ASK-2	
25	AN-G	
25	GSD-6	
21	GSD-1	
21	GSD-7	
20	MAG-1	
20	Mica-Fe	
20	SdL-1	
20?	Mica-Mg	
19.5	GSD-5	
18	GSD-4	
17	SDC-1	
17?	GL-O	
16	AGV-1	
16	GXR-4	
16?	FK-N	
15	SOIL-5	
15?	SO-4	
14	GXR-6	
14	TB	
13?	SO-2	
13?	T-1	
12.5?	SGR-1	
12	GSD-3	
12	SY-3	
12?	DT-N	
12?	SO-3	
11	BCSS-1	
11	MESS-1	
11	SCo-1	
11	SY-2	
10	GR	
10?	M-3	
9.3	GXR-1	
9	GXR-2	
8?	NBS-1645	
8?	NIM-L	
8?	NS-1	
7.8	GSP-1	
7.4	QLO-1	
7?	BCS-375	
7?	G-B	
6.4	JG-1	
6	ASK-1	
5	G-2	
5	GA	
4?	NIM-G	
3.8	GM	
3.7	GSD-8	
3?	NIM-S	
2.8	GSD-2	
2.3?	RGM-1	
1.5?	GH	
1.5?	NBS-278	
1.4	SG-1A	
1?	MA-N	
1?	STM-1	
0.5?	SS	

Table 79. Cr contents, in descending order

Cr ppm	Sample	Cr_2O_3 pct
	NBS-1645	4.33
	NIM-P	3.51
5200	IS-1	0.76
4200	DTS-1	0.61
2900	NIM-D	0.42
2800	PCC-1	0.41
2500	SW	0.37
2300	UB-N	0.34
700	VS-N	0.10
680?	NBS-697	0.10
450	BCS-395	0.07
450	MRG-1	0.07
410	ES-681-1	0.06
400	JB-1	0.06
380	BR	0.06
370?	BIR-1	0.05
360	BE-N	0.05
330	NBS-688	0.05
310	NBS-696	0.05
300	BHVO-1	0.04
300?	BX-N	0.04
270	TS	0.04
270?	DNC-1	0.04
240?	DT-N	0.04
200?	NBS-97a	0.03
200?	NBS-98a	0.03
196	NBS-1633a	0.03
195	GSD-1	0.03
190	GSD-6	0.03
160	SO-1	0.02
140	ST-1A	0.02
140?	GL-O	0.02
131	NBS-1633	0.02
130?	MO8-1	0.02
125	BCSS-1	0.02
120	BM	0.02
120	GSD-7	0.02
115?	W-1	0.02
110	GR	0.02
105	MAG-1	0.02
105	SdL-1	0.02
100	GXR-5	0.01
100	Mica-Mg	0.01
96	GXR-6	0.01
92	W-2	0.01
90	ASK-2	0.01
90	Mica-Fe	0.01
87	GSD-3	0.01
81	GSD-4	0.01
76	TB	0.01
71	MESS-1	0.01
71?	SCo-1	0.01
70	GSD-5	0.01
70?	NBS-69b	0.01
66?	SDC-1	0.01
64	GXR-4	0.01
61	SO-4	0.01
56?	M-2	0.01
55	GS-N	0.01
54?	M-3	0.01
53	JG-1	0.01
52	SGD-1A	0.01
50	AN-G	0.01
42	DR-N	0.01
40	ASK-1	0.01
37	GXR-2	0.01
33?	SGR-1	
31	NBS-81a	
30?	NIM-N	
29	SOIL-5	
26	SO-3	
26?	I-3	
25	BCS-375	
20?	T-1	
19	GXR-3	
16	SO-2	
15	BCR-1	
14?	GnA	
12.5	GSD-2	
12	GA	
12	GSP-1	
12	NIM-G	
12	NIM-S	
12	SG-1A	
12	SY-2	
10	AGV-1	
10	GXR-1	
10	SY-3	
10?	NIM-L	
10?	NS-1	
9.6	GM	
9.5?	KK	
8	G-2	
7.3	GSD-8	
7?	I-1	
6.1?	NBS-278	
6	GH	
4.2?	QLO-1	
4?	RGM-1	
4?	STM-1	
3?	BCS-313	
3?	FK-N	
3?	MA-N	
0.8?	NBS-165a	
0.8?	SS	

Table 80. Cs contents, in descending order

Cs ppm	Sample	Cs_2O pct
900?	VS-N	0.10?
640	MA-N	0.07
200	GXR-3	0.02
200?	Mica-Fe	0.02
57	SOIL-5	0.01
55?	Mica-Mg	0.01
50?	BCS-376	0.01
46	GnA	
12	SG-1A	
11	ASK-2	
11?	NBS-1633a	
11?	UB-N	
10?	JG-1	
8.6?	MAG-1	
8	NBS-1633	
8?	GM	
7.8?	SCo-1	
7	SdL-1	
7?	FK-N	
7?	TB	
6	DR-N	
6	GA	
6?	NIM-S	
5.5?	NBS-278	
5.3?	SGR-1	
5	GXR-2	
4.8	GXR-6	
4	GXR-1	
4	SGD-1A	
4?	BCSS-1	
4?	MESS-1	
4?	NIM-L	
3.9?	SDC-1	
3.3?	NS-1	
3	GXR-4	
2.5	GH	
2.5?	SY-3	
2.3?	SY-2	
2.2	GXR-5	
1.7?	QLO-1	
1.5	ASK-1	
1.5	G-1	
1.5?	STM-1	
1.4	G-2	
1.3?	AGV-1	
1.3?	BR	
1	GSP-1	
1?	JB-1	
1?	NIM-G	
1.0?	W-2	
0.96	BCR-1	
0.9	ST-1A	
0.9	W-1	
0.8?	BE-N	
0.6?	MRG-1	
0.15?	BHVO-1	
0.025?	PCC-1	
0.006	DTS-1	

Table 81. Cu contents, in descending order

Cu ppm	Sample	CuO pct
6500	GXR-4	0.81
2500	IS-1	0.31
1300	GXR-1	0.16
800	VS-N	0.10
490?	TS	0.06
380	GSD-6	0.05
360	GXR-5	0.05
340	GR	0.04
220	ST-1A	0.03
175	GSD-3	0.02
165?	I-3	0.02
140	BHVO-1	0.02
140	MA-N	0.02
135	GSD-5	0.02
135	MRG-1	0.02
130?	M-2	0.02
128	NBS-1633	0.02
125?	BIR-1	0.02
120	ASK-2	0.02
118	NBS-1633a	0.01
110	W-1	0.01
109	NBS-1645	0.01
105	GXR-6	0.01
105	W-2	0.01
100?	DNC-1	0.01
96?	NBS-688	0.01
77	SOIL-5	0.01
74?	GXR-2	0.01
72	BE-N	0.01
72	BR	0.01
68	SGD-1A	0.01
65	SGR-1	0.01
61	SO-1	0.01
59	AGV-1	0.01
56	JB-1	0.01
51	TB	0.01
50	DR-N	0.01
48?	T-1	0.01
45	BM	0.01
37	GSD-4	
37	GSD-7	
35?	MO8-1	
33	GSP-1	
31	SG-1A	
30	SdL-1	
28	SCo-1	
28	SDC-1	
28	UB-N	
27	MAG-1	
27	QLO-1	
25	MESS-1	
25?	M-3	
22	GSD-1	
22	SO-4	
20	BCS-395	
20	GS-N	
19	AN-G	
19	NIM-S	
18.5	BCSS-1	
18	GnA	
18	NIM-P	
18?	BX-N	
17	SO-3	
16	BCR-1	
16	GA	
16	SY-3	
15?	GXR-3	
14	GH	
14	NIM-N	
13	G-1	
13	GM	
13	NIM-L	
12	NIM-G	
11	RGM-1	
10	G-2	
10	NIM-D	
9?	DT-N	
8.8	KK	
8.1?	SS	
8	PCC-1	
8?	I-1	
8?	NS-1	
7	ASK-1	
7	SO-2	
7	SW	
5.9	NBS-278	
5	BCS-376	
5	DTS-1	
5	SY-2	
5?	GL-O	
4.9	GSD-2	
4.0	GSD-8	
4	JG-1	
4?	Mica-Fe	
4?	Mica-Mg	
4?	STM-1	
3	BCS-375	
3?	FK-N	

Table 82. Dy and Er contents, in descending order

Dy ppm	Sample
80?	SY-3
20?	SY-2
9?	NBS-1633
7	SdL-1
7?	BCR-1
7?	GH
5.7?	GSP-1
5?	BHVO-1
5?	SG-1A
4.2?	SCo-1
4	SOIL-5
4	W-1
4?	JB-1
4?	SGD-1A
4?	ST-1A
3.7?	BIR-1
3.5?	AGV-1
3.3	GXR-2
3.2?	JG-1
3.1	GXR-1
3.0?	DNC-1
3?	MRG-1
2.8	GXR-6
2.6	GXR-4
2.4	G-1
2.3	G-2
2.0	GXR-5
2?	NS-1
0.003	DTS-1

Er ppm	Sample
50?	SY-3
12?	SY-2
7?	SG-1A
3.5?	BCR-1
2.8?	SGD-1A
2.5?	SCo-1
2.4	W-1
2?	NS-1
2?	ST-1A
1.15?	G-1

Table 83. Eu contents, in descending order

Eu ppm	Sample	Eu ppm	Sample	Eu ppm	Sample	Eu ppm	Sample	Eu ppm	Sample
14?	SY-3	2.4?	SY-2	1.5?	JB-1	1.1?	NBS-688	0.56?	GM
6	SGD-1A	2.0	BCR-1	1.5?	MAG-1	1?	G-B	0.55?	BIR-1
4?	NBS-1633a	2.0	BHVO-1	1.5?	QLO-1	1?	NIM-L	0.54?	SGR-1
3.9?	BX-N	1.7?	SDC-1	1.4	G-2	0.94	GXR-5	0.5?	SG-1A
3.7	STM-1	1.6	GXR-4	1.4?	MRG-1	0.85?	NBS-278	0.40	GXR-3
3.7?	BR	1.6?	AGV-1	1.3	G-1	0.8	GXR-2	0.4?	NIM-G
3.6?	BE-N	1.6?	SdL-1	1.2	SOIL-5	0.78	GXR-6	0.37?	AN-G
3	ST-1A	1.6?	TB	1.2?	SCo-1	0.7?	RGM-1	0.3?	NIM-S
2.5?	NBS-1633	1.5?	DR-N	1.1	W-1	0.68	GXR-1	0.2?	NIM-P
2.4?	GSP-1	1.5?	DT-N	1.1	W-2	0.6?	NIM-N	0.002	PCC-1
				1.1?	BM	0.59?	DNC-1	0.001?	DTS-1

Table 84. Ga contents, in descending order

Ga ppm	Sample	Ga_2O_3 pct	Ga ppm	Sample	Ga ppm	Sample
400	VS-N	0.06	24?	SdL-1	17?	I-3
95	Mica-Fe	0.01	23	G-2	17?	JB-1
70?	BCS-376	0.01	23	GH	17?	M-3
70?	BX-N	0.01	23	GSP-1	16	GA
60	GnA	0.01	23?	M-2	16	NIM-N
59	MA-N	0.01	22	BCR-1	16	ST-1A
58?	NBS-1633a	0.01	22?	DR-N	16	W-1
54?	NIM-L	0.01	22?	SDC-1	16?	W-2
40	SG-1A	0.01	22?	TS	15	BM
40?	BCS-375	0.01	21	AGV-1	15	GXR-4
40?	NBS-1633	0.01	21?	BHVO-1	15?	BIR-1
37?	STM-1	0.01	21?	MAG-1	15?	DNC-1
34	GXR-5		21?	Mica-Mg	15?	JG-1
32	GXR-2		20	BR	15?	RGM-1
30	GXR-6		20	GR	14	GM
30?	DT-N		20?	T-1	14?	SCo-1
29	ASK-1		19.5	G-1	12	GXR-1
28	SY-2		19	SGD-1A	11	NIM-S
27	NIM-G		18	AN-G	8.6?	SGR-1
26	SY-3		18	SOIL-5	8?	NIM-P
25	ASK-2		18?	MRG-1	5?	UB-N
24	TB		18?	QLO-1	1?	DTS-1
24?	NS-1		17	BE-N	0.7	PCC-1

Table 85 Gd and Ge contents, in descending order

Gd ppm	Sample	Ge ppm	Sample
55?	SY-3	25?	SdL-1
35?	SOIL-5	3.3	SG-1A
10?	STM-1	2.5?	TB
9?	BE-N	1.7?	MESS-1
7.2?	SDC-1	1.6	ST-1A
6.6?	MAG-1	1.6?	GM
6.0	BHVO-1	1.5	BCR-1
5.3?	NBS-278	1.5	SGD-1A
5?	G-2	1.5?	BCSS-1
4.7?	QLO-1	1.2?	AGV-1
4.2?	SCo-1	1.1	G-1
3.5?	DR-N	1?	G-2
1.55?	BCR-1	1?	NS-1
		0.9?	DTS-1
		0.9?	GSP-1
		0.9?	PCC-1

Table 86. Hf contents, in descending order

Hf ppm	Sample	HfO_2 pct	Hf ppm	Sample
190?	NIM-L	0.02	5	BCR-1
27?	STM-1		5?	AGV-1
17?	Mica-Fe		4.8?	TB
14?	GSP-1		4.7?	GM
12?	NIM-G		4.6?	QLO-1
9.6	GXR-2		4.5?	MA-N
9?	DT-N		4.3	BHVO-1
9?	SY-3		4.3?	SCo-1
8.4?	NBS-278		4.2	SdL-1
8.1?	SDC-1		3.6?	MAG-1
8.0	GXR-4		2.7?	DR-N
8?	G-2		2.7?	W-1
8?	NBS-1633		2.6?	W-2
8?	SY-2		2.4	GXR-3
7.6?	NBS-1633a		1.6?	NBS-688
6.3	SOIL-5		1.4?	SGR-1
6.2	GXR-5		1.1	GXR-1
6.0?	RGM-1		1.0?	DNC-1
5.4?	BE-N		0.65?	BIR-1
5.3	GXR-6		0.38?	AN-G
5.2?	G-1		0.06?	PCC-1

Table 87. Hg contents, in descending order

Hg ppm	Sample	Hg ppm	Sample
3.9	GXR-1	0.082	SO-2
3.2	GXR-2	0.08	GXR-6
1.1	NBS-1645	0.044?	G-2
0.8?	SOIL-5	0.03?	SO-4
0.38	GXR-3	0.022	SO-1
0.17	GXR-5	0.017	SO-3
0.17	MESS-1	0.016?	GSP-1
0.14	NBS-1633	0.015?	AGV-1
0.13	BCSS-1	0.008?	DTS-1
0.13	GXR-4	0.007?	BCR-1
0.1?	SdL-1	0.004?	PCC-1
0.097?	G-1	0.0023?	NBS-1633a

Table 88. Ho, In and Ir contents, in descending order

Ho ppm	Sample	In ppm	Sample	Ir ppb	Sample
20?	SY-3	0.28?	NBS-1633	6?	PCC-1
2?	STM-1	0.095?	BCR-1	0.28?	W-1
1.2?	BCR-1	0.065	W-1	0.07?	G-2
1?	SG-1A	0.032?	G-2		
0.9?	SCo-1				
0.8?	SOIL-5				
0.8?	ST-1A				
0.69?	W-1				
0.5?	SGD-1A				
0.35?	G-1				

Table 89. La contents, in descending order

La ppm	Sample	La_2O_3 pct
1350	SY-3	0.16
390?	BX-N	0.05
200?	NIM-L	0.02
195	GSP-1	0.02
190?	Mica-Fe	0.02
150	STM-1	0.02
120?	M-2	0.01
105?	NIM-G	0.01
105?	NS-1	0.01
100?	G-1	0.01
92	G-2	0.01
88	SY-2	0.01
87	GSD-2	0.01
82	BE-N	0.01
82	NBS-1633	0.01
80	BR	0.01
78	SGD-1A	0.01
75?	GR	0.01
64	GXR-4	0.01
60?	M-3	0.01
56?	SO-1	0.01
53	SdL-1	0.01
47	GSD-5	0.01
45	GSD-1	0.01
45	GSD-7	0.01
44	GSD-4	0.01
42?	SDC-1	
41	GSD-3	
41	GSD-6	
41?	MAG-1	
38	GA	
36	AGV-1	
36?	JB-1	
35?	GM	
31	GSD-8	
30?	I-3	
30?	SG-1A	
29?	SCo-1	
28	SOIL-5	
27	BCR-1	
27?	QLO-1	
26?	G-B	
25	GXR-2	
25?	GH	
23?	RGM-1	
22?	JG-1	
21?	DR-N	
20?	SGR-1	
18	GXR-5	
17?	BHVO-1	
14	GXR-6	
14	ST-1A	
10.5	W-2	
10?	MRG-1	
9.8?	W-1	
9?	BM	
9?	NBS-1645	
8.5	GXR-3	
6.1	GXR-1	
3.6?	DNC-1	
3?	NIM-N	
2	AN-G	
2?	NIM-P	
1?	MA-N	
0.65?	BIR-1	

Table 90. Li contents, in descending order

Li ppm	Sample	Li_2O pct
4900	MA-N	1.05
2200	GnA	0.47
1400	Mica-Fe	0.30
500?	NBS-97a	0.11?
390	SG-1A	0.08
330	NBS-98a	0.07
175?	KK	0.04
120?	Mica-Mg	0.03
115?	TB	0.02
100	GSD-2	0.02
94?	JG-1	0.02
93	SY-2	0.02
92	SY-3	0.02
90	GA	0.02
78?	MAG-1	0.02
70?	BCS-375	0.02
70?	BM	0.02
70?	GL-O	0.02
55?	GR	0.01
55?	GS-N	0.01
52?	SOIL-5	0.01
51	GM	0.01
51	GSD-4	0.01
50?	BCS-309	0.01
50?	RGM-1	0.01
48?	NIM-L	0.01
45	GSD-5	0.01
45?	GH	0.01
44?	SCo-1	0.01
43?	TS	0.01
42	DR-N	0.01
40	GSD-6	0.01
40?	SO-1	0.01
35	G-2	0.01
33	GSD-3	0.01
32	GSD-7	0.01
32?	SDC-1	0.01
30	ASK-2	0.01
30	GSD-1	0.01
30	GSP-1	0.01
30?	STM-1	0.01
29?	SdL-1	0.01
28?	UB-N	0.01
23?	QLO-1	
22?	G-1	
21?	NS-1	
20?	BCS-313	
20?	BCS-376	

Li ppm	Sample
20?	I-3
18	ASK-1
14.5?	W-1
14	BCR-1
14	SGD-1A
14	ST-1A
13.5	GSD-8
13	AN-G
13	BR
12	AGV-1
12	BE-N
12?	NIM-G
11?	JB-1
9.6?	W-2
9?	SO-2
6?	NIM-N
5.2?	DNC-1
4.7?	SS
4	MRG-1
4?	BHVO-1
4?	NIM-D
3.6?	BIR-1
3?	PCC-1
2?	DTS-1
2?	NIM-S

Table 91. Lu contents, in descending order

Lu ppm	Sample
8?	SY-3
3?	SY-2
2?	NIM-G
1?	NBS-1633
0.75?	NBS-278
0.55?	TB
0.5?	BCR-1
0.5?	SdL-1
0.4?	BM
0.4?	GM
0.35?	W-1
0.34	SOIL-5
0.34?	NBS-688
0.33?	W-2
0.32?	DNC-1
0.3?	AGV-1
0.3?	JB-1
0.29?	BIR-1
0.24?	BE-N
0.2?	GSP-1
0.2?	MRG-1
0.19?	G-1
0.12?	AN-G
0.1	G-2
0.006?	PCC-1

Table 92. Mo contents, in descending order

Mo ppm	Sample	MoO_3 pct
700?	VS-N	0.11
310	GXR-4	0.05
130?	TS	0.02
100	GnA	0.02
93	GSD-3	0.01
60	ASK-2	0.01
57	IS-1	0.01
36?	SGR-1	0.01
30	GXR-5	
29?	NBS-1633a	
23?	NBS-1633	
20?	JB-1	
18?	GR	
18?	GXR-1	
7.8	GSD-6	
6.5?	G-1	
5.2	STM-1	
4?	NIM-L	
3?	AGV-1	
3?	BR	
3?	GH	
3?	NIM-G	
3?	SY-2	
2.6?	QLO-1	
2.5?	SY-3	
2.3?	RGM-1	
2.2?	MESS-1	
2.0	GSD-2	
2?	JG-1	
2?	NS-1	
2?	SO-2	
2?	SOIL-5	
1.9?	BCSS-1	
1.8	ST-1A	
1.7	GXR-6	
1.5	SGD-1A	
1.5?	BCR-1	
1.5?	GSP-1	
1.4	GSD-7	
1.4?	SCo-1	
1.3	SG-1A	
1.3?	SdL-1	
1.1	GSD-5	
1.1?	GM	
1	GA	
1?	BHVO-1	
1?	DTS-1	
1?	MAG-1	
0.9?	G-2	
0.82	GSD-4	
0.74	GSD-1	
0.57?	W-1	
0.52	GSD-8	
0.5?	PCC-1	

Table 93. N contents, in descending order.

N ppm	Sample	N pct
4000?	SO-4	0.40?
2200?	SO-2	0.20?
797	NBS-1645	0.08
400?	SO-1	0.04?
59?	G-1	0.01
56?	G-2	0.01
52?	W-1	0.01
48?	GSP-1	
43?	AGV-1	
43?	PCC-1	
30?	BCR-1	
27?	DTS-1	

Table 94. Nb contents, in descending order

Nb ppm	Sample	Nb_2O_5 pct
960	NIM-L	0.14
380	SG-1A	0.05
270?	Mica-Fe	0.04
270?	STM-1	0.04
195?	NS-1	0.03
175	MA-N	0.03
130	SY-3	0.02
120?	Mica-Mg	0.02
100	BE-N	0.01
100?	BR	0.01
96	GSD-2	0.01
90?	GnA	0.01
85?	GH	0.01
53	NIM-G	0.01
36	GSD-1	0.01
35	GSD-8	0.01
24	G-1	
23?	GSP-1	
23?	SY-2	
20?	MRG-1	
19.5	GSD-5	
19	BHVO-1	
19?	BCR-1	
18.5	GSD-4	
18.5?	SDC-1	
17?	GM	
16.5	GSD-3	
16.5	GSD-7	
16?	AGV-1	
13?	G-2	
12	GSD-6	
10.5?	QLO-1	
10?	GA	
10?	SCo-1	
9.6?	MAG-1	
9.5	W-1	
9.4?	RGM-1	
9?	SOIL-5	
8	SGD-1A	
8	ST-1A	
6.8?	W-2	
6?	DR-N	
5.3?	SGR-1	
3.2?	DNC-1	
2.3?	BIR-1	
2?	AN-G	
1?	PCC-1	

Table 95. Nd contents, in descending order

Nd ppm	Sample	Nd_2O_3 pct
800?	SY-3	0.09
190?	GSP-1	0.02
78	STM-1	0.01
71?	NS-1	0.01
71?	SY-2	0.01
70	BE-N	0.01
68?	NIM-G	0.01
66?	SGD-1A	0.01
62?	NBS-1633	0.01
60?	BR	0.01
58?	G-2	0.01
56	G-1	0.01
48?	DT-N	0.01
45?	NIM-L	0.01
44	SdL-1	0.01
41	MAG-1	
38	SDC-1	
37?	AGV-1	
30	SOIL-5	
27	SCo-1	
26?	BCR-1	
25?	GA	
25?	GH	
24	BHVO-1	
23?	QLO-1	
22?	DR-N	
21?	JB-1	
19?	MRG-1	
19?	RGM-1	
18	SG-1A	
15	SGR-1	
15	W-1	
13.5?	W-2	
9	ST-1A	
6?	NIM-S	
5.2?	DNC-1	
2?	AN-G	

Table 96. Ni contents, in descending order

Ni ppm	Sample	NiO pct
2400	PCC-1	0.31
2300	DTS-1	0.29
2200	SW	0.28
2000	NIM-D	0.25
2000	UB-N	0.25
800	VS-N	0.10
640	IS-1	0.08
560	NIM-P	0.07
270	BE-N	0.03
260	BR	0.03
250	DNC-1	0.03
200?	BX-N	0.03
195	MRG-1	0.02
185	TS	0.02
165?	BIR-1	0.02
160	ES-681-1	0.02
150	ASK-2	0.02
150?	NBS-688	0.02
135	JB-1	0.02
127	NBS-1633a	0.02
120	BHVO-1	0.02
120	NIM-N	0.02
110	ASK-1	0.01
110	Mica-Mg	0.01
98	NBS-1633	0.01
94	SO-1	0.01
90	ST-1A	0.01
79	GSD-6	0.01
76	GSD-1	0.01
76?	W-1	0.01
70	W-2	0.01
63	GXR-5	0.01
56	BM	0.01
55	BCSS-1	0.01
55	GR	0.01
55	GXR-3	0.01
54	GSD-7	0.01
54	MAG-1	0.01
50	SGD-1A	0.01
50?	MO8-1	0.01
45.8	NBS-1645	0.01
45	SdL-1	0.01
42	GXR-1	0.01
40	GSD-4	0.01
39	TB	
38	GXR-4	
36	SDC-1	
36?	GL-O	
36?	M-2	
35	AN-G	
35	Mica-Fe	
34	GSD-5	
34	GS-N	
34	SGR-1	
32	BCS-395	
30	MESS-1	
30	SCo-1	
26	GSD-3	
26	SO-4	
22	GXR-6	
18	GXR-2	
17?	I-3	
17?	M-3	
16	DR-N	
16	SO-3	
16?	DT-N	
15	AGV-1	
13?	SOIL-5	
12?	SO-2	
11	SG-1A	
11	SY-3	
11?	NIM-L	
10	BCR-1	
10	SY-2	
10?	T-1	
9	GSP-1	
8.2	JG-1	
8?	NIM-G	
7.4	GM	
7	GA	
7?	NIM-S	
7?	NS-1	
6?	RGM-1	
5.5	GSD-2	
5.5?	QLO-1	
3.6	NBS-278	
3.5	G-2	
3	GH	
3.0	GSD-8	
3?	FK-N	
3?	MA-N	
3?	STM-1	
2.6?	SS	

Table 97. Os content

Os ppb	Sample
9?	PCC-1

Table 98. Pb Contents, in descending order.

Pb ppm	Sample	PbO pct	Pb ppm	Sample	PbO pct	Pb ppm	Sample	Pb ppm	Sample
1000	VS-N	0.11	48?	G-1	0.01	26	JG-1	14	SO-3
900	NBS-91	0.10	45	GH		24	GSD-1	13?	Mica-Fe
714	NBS-1645	0.08	43	NIM-L		24?	MAG-1	11.5	BM
670	GXR-1	0.07	41	GSD-3		23	BCSS-1	11.5	JB-1
620	GXR-2	0.07	41?	SGR-1		23?	SDC-1	11	DTS-1
350	GSD-7	0.04	40	NIM-G		22	GXR-5	11	PCC-1
240	FK-N	0.03	38	SdL-1		21	GSD-8	10	MRG-1
230	SG-1A	0.02	37?	T-1		21	SO-1	10?	I-3
135?	BX-N	0.01	35?	MO8-1		21	SO-2	9?	Mica-Mg
130	SOIL-5	0.01	34	MESS-1		21?	QLO-1	8	BCS-375
130	SY-3	0.01	33	AGV-1		21?	RGM-1	8	BR
120	KK	0.01	33?	TS		20?	GnA	7.8?	W-1
115	GSD-5	0.01	32	GR		20?	M-3	7	TB
110	GXR-6	0.01	31	GSD-2		19?	SW	7?	NIM-D
80	SY-2	0.01	31	GSD-4		18	SGD-1A	7?	NIM-N
74?	I-1	0.01	30	G-2		18	UB-N	7?	NS-1
72.4	NBS-1633a	0.01	30	GA		18?	STM-1	6	ST-1A
70	NBS-1633	0.01	29	MA-N		17?	FK	6?	NIM-P
70?	ES-681-1	0.01	28	BCS-395		17?	M-2	5.7?	SS
61	BCS-376	0.01	28	GM		16	NBS-278	5?	NIM-S
60	GS-N	0.01	28	GSD-6		16	SO-4	4?	BE-N
55	DR-N	0.01	28?	DT-N		15	GXR-3	3.3	NBS-688
54	GSP-1	0.01	28?	SCo-1		14	BCR-1	2?	AN-G
								0.16	IS-1

Table 99. Pr, Pt and Ra concentrations

Pr ppm	Sample	Pr_6O_{11} pct	Pt ppb	Sample	Ra ppt	Sample
120?	SY-3	0.01	10?	PCC-1	0.7?	AGV-1
20?	NS-1				0.7?	G-2
19?	G-2				0.7?	GSP-1
10?	SGD-1A				0.6?	BCR-1
7?	BCR-1				0.0018?	PCC-1
5?	SOIL-5				0.0013?	DTS-1
3?	SG-1A					
2	ST-1A					

Table 100. Rb contents, in descending order

Rb ppm	Sample	Rb_2O pct	Rb ppm	Sample	Rb_2O pct	Rb ppm	Sample	Rb_2O pct
3600	MA-N	0.39	175	TB	0.02	75?	SO-4	0.01
2200	Mica-Fe	0.24	170	G-2	0.02	74	QLO-1	0.01
2000	GnA	0.22	160?	KK	0.02	73	SGD-1A	0.01
1300	Mica-Mg	0.14	155?	RGM-1	0.02	70	DR-N	0.01
1100	SG-1A	0.12	150	MAG-1	0.02	67	AGV-1	0.01
850?	FK-N	0.09	145	GSD-7	0.02	48	BCS-375	0.01
800?	VS-N	0.09	145?	SO-1	0.02	47	BCR-1	0.01
550?	NBS-70a	0.06	140	SOIL-5	0.02	47	BE-N	0.01
530	NIM-S	0.06	135?	FK	0.01	47	BR	0.01
480	GSD-2	0.05	131	NBS-1633a	0.01	47?	DNC-1	0.01
390	GH	0.04	130	GSD-4	0.01	42?	I-3	
370	BCS-376	0.04	130	GSD-8	0.01	41	JB-1	
320	NIM-G	0.03	130?	I-1	0.01	41?	SO-3	
310?	M-2	0.03	128	NBS-278	0.01	40	GXR-5	
250	GM	0.03	120	GSD-5	0.01	32?	T-1	
250	GSP-1	0.03	120?	SDC-1	0.01	29	GXR-1	
240	GL-O	0.03	120?	STM-1	0.01	25?	M-3	
220	G-1	0.02	115	GSD-1	0.01	21	W-1	
220	SY-2	0.02	115	GXR-3	0.01	21	W-2	
220?	TS	0.02	115	NBS-1633	0.01	16	ST-1A	
210	NS-1	0.02	115	SCo-1	0.01	12.5	BM	
208	SY-3	0.02	115	SdL-1	0.01	10	BHVO-1	
190	NIM-L	0.02	105	GSD-6	0.01	8	MRG-1	
190?	GS-N	0.02	105	GXR-6	0.01	6?	NIM-N	
185	JG-1	0.02	86	GXR-2	0.01	6?	UB-N	
175	ASK-2	0.02	85	ASK-1	0.01	5?	NIM-P	
175	GA	0.02	81?	SGR-1	0.01	1.9	NBS-688	
175	GR	0.02	81?	SO-2	0.01	1?	AN-G	
175	GXR-4	0.02	78	GSD-3	0.01	0.3?	PCC-1	
						0.05?	DTS-1	

Table 101. Re, Rh and Ru contents, in descending order

Re ppb	Sample	Rh ppb	Sample	Ru ppb	Sample
0.08	BCR-1	1?	PCC-1	9.5?	PCC-1
0.07?	PCC-1	0.9?	DTS-1		
		0.2?	BCR-1		

Table 102. Sb contents, in descending order

Sb ppm	Sample	Sb_2O_3 pct	Sb ppm	Sample	Sb ppm	Sample
800?	VS-N	0.11?	2	GXR-5	0.73	MESS-1
125	GXR-1	0.02	2.0?	BM	0.6	BCR-1
51?	NBS-1645	0.01	2?	QLO-1	0.59	BCSS-1
48	GXR-2	0.01	1.9	GSD-4	0.54?	SDC-1
40	GXR-3	0.01	1.9?	MA-N	0.5?	BIR-1
14	SOIL-5		1.7?	STM-1	0.5?	DTS-1
7	NBS-1633		1.5?	NBS-278	0.5?	GM
7?	NBS-1633a		1.4?	PCC-1	0.5?	GSD-2
5.6	GSD-3		1.3	SdL-1	0.4	MRG-1
4.4	GXR-4		1.3?	RGM-1	0.31?	G-1
4.3?	AGV-1		1.3?	SG-1A	0.3	SY-3
4.1	GSD-5		1.1?	GSD-6	0.3?	DR-N
3.8	GXR-6		1	ST-1A	0.26?	UB-N
3.5?	SGR-1		1.0	W-1	0.22?	GSD-8
3.3?	TB		1.0?	DNC-1	0.2	SY-2
3.1?	GSP-1		1?	MAG-1	0.2?	DT-N
2.7	GSD-7		1?	SGD-1A	0.2?	GSD-1
2.5?	SCo-1		0.85?	W-2	0.17?	BHVO-1
					0.06?	G-2

Table 103. Sc contents, in descending order

Sc ppm	Sample	Sc_2O_3 pct	Sc ppm	Sample	Sc ppm	Sample
300?	VS-N	0.05?	26?	BR	7?	NIM-D
60?	BX-N	0.01	22	BE-N	7?	SY-2
50?	I-3	0.01	22?	TS	7?	SY-3
48?	MRG-1	0.01	19?	SO-1	6.8	GXR-2
43	ST-1A	0.01	18	GXR-3	6.6	GSP-1
43?	BIR-1	0.01	17	MAG-1	5.1?	NBS-278
40?	NBS-1633a	0.01	17	SdL-1	5	SG-1A
38?	NBS-688	0.01	15	SOIL-5	5?	GM
38?	NIM-N	0.01	15?	SDC-1	5?	SGR-1
36?	W-2	0.01	14	TB	4.7	RGM-1
35?	W-1	0.01	13.5?	UB-N	4?	NIM-S
34	BM	0.01	12.5	AGV-1	3.8	DTS-1
33	BCR-1	0.01	11?	SCo-1	3.5	G-2
31	BHVO-1		10	AN-G	2.9?	G-1
31	DNC-1		9?	GnA	2.3?	DT-N
31	GXR-6		9?	PCC-1	2?	NBS-1645
30?	M-2		9?	QLO-1	1.7	GXR-1
29?	NIM-P		8.3	GXR-4	1?	GH
28?	DR-N		7.8	GXR-5	1?	NIM-G
27	NBS-1633		7	ASK-1	0.7?	STM-1
27	SGD-1A		7	GA	0.3?	NIM-L
			7?	GR	0.24?	MA-N

Table 104. Se contents, in descending order

Se ppm	Sample
18.5	GXR-1
10.3	NBS-1633a
9.4	NBS-1633
6.0	GXR-4
3.4?	SGR-1
3?	SdL-1
1.1	GXR-5
1.05	GXR-6
1?	SOIL-5
0.74	GXR-2
0.4?	BCSS-1
0.4?	MESS-1
0.22	GXR-3
0.1?	BCR-1

Table 105. Sm contents, in descending order

Sm ppm	Sample	Sm_2O_3 pct
100?	SY-3	0.01
25?	GSP-1	
17	SGD-1A	
16?	NIM-G	
15?	SY-2	
13	STM-1	
12	BE-N	
12	NBS-1633	
12?	BR	
10?	GH	
10?	NS-1	
9	SdL-1	
8.7?	TB	
8.3?	G-1	
8.3?	SDC-1	
8.1?	MAG-1	
7.2	G-2	
7	SG-1A	
6.5	BCR-1	
6.1	BHVO-1	
6	GXR-4	
5.9	AGV-1	
5.7?	NBS-278	
5.4	SOIL-5	
5.3?	DR-N	
5.1?	QLO-1	
5.1?	SCo-1	
5?	GA	
5?	GM	
5?	MRG-1	
4.8?	JB-1	
4.6?	G-B	
4.6?	JG-1	
4.3?	RGM-1	
4	ST-1A	
3.7?	BM	
3.6?	W-1	
3.3	GXR-2	
3.3?	W-2	
2.9	GXR-5	
2.8?	NBS-688	
2.8?	SGR-1	
2.4	GXR-6	
1.4?	DNC-1	
1.0	GXR-3	
1.0?	BIR-1	
0.7?	AN-G	

Table 106. Sn contents, in descending order

Sn ppm	Sample	SnO_2 pct
1900	GnA	0.24
1050?	MA-N	0.13?
800?	VS-N	0.10?
70?	Mica-Fe	0.01
33?	KK	
29	GSD-2	
11	SG-1A	
10?	GH	
10?	GR	
10?	NBS-1633	
9.2	GSD-8	
9?	STM-1	
8?	BR	
7?	NIM-L	
6.4	SW	
6?	SY-3	
6?	TB	
5.3	GSD-7	
5.2?	MAG-1	
5?	GSP-1	
4.6	GSD-5	
4.5	GM	
4.0	GSD-4	
4	SY-2	
4?	GA	
4?	JG-1	
4?	NIM-G	
3.7	SGD-1A	
3.7?	SCo-1	
3.6	AGV-1	
3.5	G-1	
3.5	ST-1A	
3.5?	NS-1	
3.2	MRG-1	
3.2	W-1	
3.0	GSD-3	
2.8	GSD-1	
2.8	GSD-6	
2.5	BCR-1	
2?	JB-1	
2?	NIM-D	
1.7?	BM	
1.7?	DTS-1	
1.6?	PCC-1	
1.4?	G-2	
0.19	IS-1	

Table 107. Sr contents, in descending order

Sr ppm	Sample	SrO pct	Sr ppm	Sample	SrO pct	Sr ppm	Sample	SrO pct
4600	NIM-L	0.54	280	GXR-1	0.03	105?	BIR-1	0.01
2300	SGD-1A	0.27	275	SY-2	0.03	100	ASK-2	0.01
1500	NBS-97a	0.18	270	ST-1A	0.03	100	RGM-1	0.01
1400	NBS-1633	0.17	260	GSD-6	0.03	96?	BCSS-1	0.01
1350	BE-N	0.16	260	I-3	0.03	93?	TS	0.01
1300	BR	0.15	260	MRG-1	0.03	91	GSD-3	0.01
1150	GXR-3	0.14	260	NIM-N	0.03	89?	MESS-1	0.01
1150	NS-1	0.14	250	G-1	0.03	84	MA-N	0.01
830	NBS-1633a	0.10	240	GSP-1	0.03	80?	SdL-1	0.01
700	STM-1	0.08	230	BM	0.03	76	AN-G	0.01
700?	VS-N	0.08?	220	GSD-7	0.03	76?	KK	0.01
680	ASK-1	0.08	220	GXR-4	0.03	64	BCS-375	0.01
660	AGV-1	0.08	220	SO-3	0.03	63.5	NBS-278	0.01
570	GS-N	0.07	200	GSD-5	0.02	62	NIM-S	0.01
550	GR	0.07	190	W-1	0.02	55	BCS-376	0.01
520	GSD-1	0.06	190?	W-2	0.02	52	GSD-8	0.01
500?	M-3	0.06	185	JG-1	0.02	42	GXR-6	
480	G-2	0.06	185?	M-2	0.02	35?	FK-N	
440	JB-1	0.05	180	SDC-1	0.02	32	NIM-P	
430	SGR-1	0.05	170	I-1	0.02	27	GSD-2	
420	BHVO-1	0.05	170	SCo-1	0.02	27?	DT-N	
400	DR-N	0.05	170	SO-4	0.02	25	Mica-Mg	
390?	T-1	0.05	169	NBS-688	0.02	23	BCS-395	
350	QLO-1	0.04	160	GXR-2	0.02	20	SG-1A	
340	SO-2	0.04	150	TB	0.02	19	GL-O	
330	BCR-1	0.04	145?	DNC-1	0.02	10	GH	
330	NBS-98a	0.04	140	GSD-4	0.02	10	NIM-G	
330?	SOIL-5	0.04	140	MAG-1	0.02	10	UB-N	
310	GA	0.04	135	GM	0.02	5	Mica-Fe	
306	SY-3	0.04	120	GXR-5	0.01	3?	NIM-D	
300?	SO-1	0.04	110?	BX-N	0.01	0.4	PCC-1	
						0.4?	DTS-1	

Table 108. Ta contents, in descending order

Ta ppm	Sample	Ta_2O_5 pct	Ta ppm	Sample	Ta ppm	Sample
310?	MA-N	0.04	1.5	G-1	0.8?	G-2
34?	Mica-Fe		1.4?	AGV-1	0.77	GXR-4
26	SG-1A		1.3?	SDC-1	0.76	GXR-2
22?	NIM-L		1.2	ST-1A	0.76	SOIL-5
18?	STM-1		1.2?	NBS-278	0.7?	DR-N
11?	NS-1		1.1	SGD-1A	0.52	GXR-6
5.5?	BE-N		1.1?	BHVO-1	0.50	W-1
4.5?	NIM-G		1.1?	MAG-1	0.5?	SGR-1
4?	BX-N		1?	GSP-1	0.5?	W-2
2.7?	DT-N		1.0?	RGM-1	0.46	GXR-5
2?	NBS-1633		0.9?	QLO-1	0.32	GXR-3
1.6?	SdL-1		0.9?	SCo-1	0.2	GXR-1
1.6?	TB		0.8?	BCR-1	0.2?	AN-G

Table 109. Tb contents, in descending order

Tb ppm	Sample	Tb ppm	Sample	Tb ppm	Sample	Tb ppm	Sample	Tb ppm	Sample
11?	SY-3	1.4?	GSP-1	1.0?	BHVO-1	0.75?	QLO-1	0.54	G-1
3?	NIM-G	1.4?	SdL-1	1.0?	MAG-1	0.7?	AGV-1	0.5?	G-2
2?	NBS-1633	1.3?	BE-N	1.0?	NBS-278	0.7?	NIM-L	0.45?	NBS-688
2?	SY-2	1.2?	SDC-1	0.8?	DR-N	0.66	SOIL-5	0.4?	DNC-1
1.6?	STM-1	1.0	BCR-1	0.8?	SCo-1	0.65	W-1	0.35?	SGR-1
						0.65?	W-2	0.2?	AN-G

Table 110. Th contents, in descending order

Th ppm	Sample	ThO$_2$ pct	Th ppm	Sample	Th ppm	Sample
990	SY-3	0.11	15.5	GSD-5	8.3	GXR-2
380?	SY-2	0.04	15?	RGM-1	6.4	AGV-1
150?	Mica-Fe	0.02	14.5	GSD-4	6.1	BCR-1
120	SG-1A	0.01	14	SdL-1	5.3	GXR-5
105	GSP-1	0.01	14?	G-B	5.2	GXR-6
90?	GH	0.01	13.5	GSD-8	5	DR-N
67	GSD-2	0.01	13.5	JG-1	4.9?	SGR-1
65	NIM-L	0.01	13.5?	DT-N	4.8?	QLO-1
55?	BX-N	0.01	12.5?	MAG-1	3?	BM
52	NIM-G	0.01	12	GSD-7	3?	ST-1A
50	G-1	0.01	12	NBS-278	2.9	GXR-3
40?	GnA		12?	BR	2.4	W-1
35?	GM		12?	SDC-1	2.4?	W-2
31?	STM-1		11	BE-N	2.3	GXR-1
26	GSD-1		11	SOIL-5	1.62	NBS-1645
25	G-2		9.6?	SCo-1	1.0	BHVO-1
24.7	NBS-1633a		9.3	GSD-6	1?	MA-N
24?	NBS-1633		9	SGD-1A	1?	MRG-1
22	GXR-4		9?	JB-1	1?	NIM-P
19?	TB		9?	NS-1	0.9?	NIM-S
17	GA		8.9	GSD-3	0.8?	NIM-D
					0.3	NBS-688

Table 111. Tl and Tm contents, in descending order

Tl ppm	Sample	Tm ppm	Sample
5.7	NBS-1633a	8?	SY-3
4?	NBS-1633	2?	SY-2
1.6	AGV-1	0.7?	SDC-1
1.44	NBS-1645	0.6?	BCR-1
1.3?	GSP-1	0.5?	SCo-1
1.25?	G-1	0.4?	SOIL-5
1.2?	G-2	0.4?	W-2
0.7?	MESS-1	0.30	W-1
0.6?	BCSS-1	0.3?	BHVO-1
0.54	NBS-278	0.3?	DNC-1
0.3?	BCR-1	0.15	G-1
0.11	W-1	0.1?	MRG-1

Table 112. U contents, in descending order

U ppm	Sample	U_3O_8 pct	U ppm	Sample	U ppm	Sample
650	SY-3	0.07	4.0	SdL-1	2.1	GSP-1
290	SY-2	0.03	4?	GA	2.1	GXR-5
63	SG-1A	0.01	4?	NS-1	2.0?	QLO-1
60?	Mica-Fe	0.01	4?	SGD-1A	1.95	AGV-1
35	GXR-1		3.4?	G-1	1.8	GSD-3
22?	GnA		3.3	JG-1	1.8	JB-1
22?	TS		3.2	GSD-7	1.7	BCR-1
18?	GH		3.2	SOIL-5	1.60	GXR-6
15.5	GSD-2		3.1	GSD-8	1.5	DR-N
15?	NIM-G		3.1	GXR-3	1.11	NBS-1645
14	NIM-L		3.0	GXR-2	0.7?	ST-1A
12?	MA-N		3?	BR	0.6?	NIM-N
11.6	NBS-1633		3.0?	SDC-1	0.6?	NIM-S
10.2	NBS-1633a		2.9?	SCo-1	0.58?	W-1
9.1?	STM-1		2.8?	MAG-1	0.5?	Mica-Mg
8?	BX-N		2.4	BE-N	0.4?	BHVO-1
6.4	GXR-4		2.4	GSD-5	0.4?	NIM-P
5.8?	RGM-1		2.3	GSD-4	0.37?	NBS-688
5.4?	SGR-1		2.3?	DT-N	0.3?	MRG-1
4.6	NBS-278		2.2	GSD-6	0.005?	PCC-1
4.3	GSD-1		2.1	G-2	0.004?	DTS-1

Table 113. V contents, in descending order

V ppm	Sample	V_2O_5 pct	V ppm	Sample	V_2O_5 pct	V ppm	Sample	V_2O_5 pct
930?	TS	0.17	150?	SOIL-5	0.03	62?	GS-N	0.01
770	ES-681-1	0.14	140	GSD-6	0.02	61	QLO-1	0.01
600?	VS-N	0.11?	140	MAG-1	0.02	60	GXR-5	0.01
520	MRG-1	0.09	140	SO-1	0.02	57	GXR-2	0.01
500?	I-3	0.09?	135?	Mica-Fe	0.02	54	GSP-1	0.01
420	BCR-1	0.07	135?	SCo-1	0.02	52	SY-2	0.01
390?	NBS-696	0.07	130?	MO8-1	0.02	51	NS-1	0.01
390?	NBS-697	0.07	125	AGV-1	0.02	51	SY-3	0.01
320	ST-1A	0.06	125	SGR-1	0.02	49	ASK-1	0.01
320?	BHVO-1	0.06	120	GSD-1	0.02	44?	SO-3	0.01
310	BIR-1	0.06	120	GSD-3	0.02	40	NIM-D	0.01
310?	BX-N	0.06	120	GSD-4	0.02	39	GXR-3	0.01
300?	NBS-1633a	0.05	110	GSD-5	0.02	38	GA	0.01
260	W-2	0.05	105	TB	0.02	36	G-2	0.01
260?	W-1	0.05	105?	SDC-1	0.02	29	PCC-1	0.01
250?	NBS-688	0.04	96	GSD-7	0.02	26	GSD-8	0.01
240	BE-N	0.04	96?	T-1	0.02	24	JG-1	
240	BR	0.04	93	BCSS-1	0.02	23.5	NBS-1645	
240	SGD-1A	0.04	92	GXR-4	0.02	19?	SW	
230	DR-N	0.04	90	SO-4	0.02	17?	G-1	
230	NIM-P	0.04	90?	Mica-Mg	0.02	16	GSD-2	
220	ASK-2	0.04	88	GXR-1	0.02	14?	RGM-1	
220	NIM-N	0.04	81	NIM-L	0.01	11	DTS-1	
214	NBS-1633	0.04	80?	M-2	0.01	11	GM	
210	JB-1	0.04	77?	IS-1	0.01	10	NIM-S	
180	BM	0.03	75	UB-N	0.01	7?	I-1	
180	GXR-6	0.03	75?	M-3	0.01	5	SG-1A	
170	SdL-1	0.03	72	MESS-1	0.01	5?	GH	
170?	NBS-69b	0.03	70	AN-G	0.01	4.6?	MA-N	
160?	DT-N	0.03	65	GR	0.01	2?	NIM-G	
150	DNC-1	0.03	64	SO-2	0.01	1.4?	SS	

Table 114. W contents, in descending order

W ppm	Sample	WO_3 pct	W ppm	Sample	W ppm	Sample
	GXR-3	1.36	6?	SdL-1	2.4	GSD-4
520?	GnA	0.07	5.6	GSD-7	2.3	SG-1A
90?	AN-G	0.01	5.0	GSD-3	1.9	GSD-8
70?	MA-N	0.01	5?	SOIL-5	1.8	GXR-2
29?	BE-N		4	NBS-1633	1.6?	RGM-1
28	GXR-4		3.8?	STM-1	1.0	GSD-1
25	GSD-6		3.2	GSD-5	0.88	GXR-6
24	GSD-2		3?	TB	0.8?	SDC-1
					0.4?	BCR-1

Table 115. Y contents, in descending order

Y ppm	Sample	Y_2O_3 pct	Y ppm	Sample	Y ppm	Sample
740	SY-3	0.09	30	SGD-1A	21	GA
180?	TS	0.02	30?	DR-N	21	GSD-6
145	NIM-G	0.02	30?	ST-1A	21?	SOIL-5
130	SY-2	0.02	29	GSP-1	20?	NIM-S
120?	BX-N	0.02	27	GSD-4	19	AGV-1
85?	SdL-1	0.01	27?	BHVO-1	19?	GR
70	GH	0.01	27?	MAG-1	18?	DNC-1
69	SG-1A	0.01	26	GSD-5	17	GSD-8
67	GSD-2	0.01	26?	BM	17?	NS-1
66?	NBS-1633	0.01	26?	GM	17?	SO-3
60?	M-2	0.01	26?	JB-1	16?	BIR-1
50?	I-3	0.01	25	W-1	16?	MRG-1
46?	STM-1	0.01	25?	Mica-Fe	13	G-1
45?	M-3	0.01	25?	NIM-L	13?	FK-N
42?	SDC-1	0.01	25?	RGM-1	13?	G-B
40	BCR-1	0.01	24?	QLO-1	13?	SGR-1
40?	SO-2	0.01	24?	SCo-1	11	G-2
39?	TB		24?	SO-1	11?	UB-N
31?	JG-1		23	GSD-7	8	AN-G
30	BE-N		23?	SO-4	6?	NIM-N
30	BR		23?	W-2	6?	NIM-P
			22	GSD-1	1?	MA-N
			22	GSD-3		

Table 116. Yb contents, in descending order

Yb ppm	Sample	Yb_2O_3 pct	Yb ppm	Sample	Yb ppm	Sample
900?	VS-N	0.10?	3?	G-B	2?	BR
65	SY-3	0.01	2.9	SGD-1A	2.0?	DNC-1
17	SY-2		2.9?	GM	2?	GA
14	NIM-G		2.8?	DR-N	1.9	AGV-1
8?	GH		2.7	GXR-6	1.9	GSP-1
7?	NBS-1633		2.6	MAG-1	1.8	BE-N
6	SG-1A		2.5	QLO-1	1.8	GXR-1
4.5?	NBS-278		2.5	RGM-1	1.8	GXR-4
4.3	STM-1		2.2	GXR-2	1.7?	BIR-1
4.2	SDC-1		2.2	SCo-1	1.5?	JG-1
4	ST-1A		2.2	SOIL-5	1.05?	G-1
4?	NIM-L		2.1	W-1	1.0	SGR-1
4?	TB		2.1	W-2	1?	MRG-1
3.5?	BM		2.1?	JB-1	0.86	G-2
3.4	BCR-1		2.1?	NBS-688	0.85	AN-G
3	SdL-1		2	GR	0.8?	NIM-N
			2.0	GXR-5	0.76	GXR-3

Table 117. Zn contents, in descending order

Zn ppm	Sample	ZnO pct
1720	NBS-1645	0.21
1300	Mica-Fe	0.16
800	VS-N	0.10
740	GXR-1	0.09
640?	NBS-91	0.08
500	GXR-2	0.06
400	NIM-L	0.05
370	SOIL-5	0.05
320?	NBS-697	0.04
290	Mica-Mg	0.04
270	SG-1A	0.03
250	SY-2	0.03
240	GSD-5	0.03
240	GSD-7	0.03
240	STM-1	0.03
240	SY-3	0.03
220	GXR-3	0.03
220	MA-N	0.03
220	NBS-1633a	0.03
220	SdL-1	0.03
210	NBS-1633	0.03
190	MESS-1	0.02
190	MRG-1	0.02
180?	T-1	0.02
165	ASK-2	0.02
150	BR	0.02
150	ST-1A	0.02
145	DR-N	0.02
145	GSD-6	0.02
145	SO-1	0.02
135	MAG-1	0.02
130?	M-2	0.02
125	BCR-1	0.02
125	SO-2	0.02
120	BCSS-1	0.01
120	BE-N	0.01
120	GXR-6	0.01
120	SGD-1A	0.01
115	BM	0.01
105	ASK-1	0.01
105	BHVO-1	0.01
105	GSP-1	0.01
105	SCo-1	0.01
105	SDC-1	0.01
100	GSD-4	0.01
100	NIM-P	0.01
100?	I-3	0.01
94	SO-4	0.01
93	TB	0.01
92?	UB-N	0.01
90	NIM-D	0.01
89?	TS	0.01
86	AGV-1	0.01
86	W-1	0.01
85	GH	0.01
84	G-2	0.01
84	JB-1	0.01
81	SGR-1	0.01
80	GA	0.01
80	W-2	0.01
79	GSD-1	0.01
76	GnA	0.01
74	SS	0.01
70	DNC-1	0.01
70?	BIR-1	0.01
70?	NS-1	0.01
68	NIM-N	0.01
64	GXR-4	0.01
64	QLO-1	0.01
60	GR	0.01
60?	BX-N	0.01
58	SW	0.01
58?	NBS-688	0.01
55?	NBS-278	0.01
52	GSD-3	0.01
52	SO-3	0.01
50	GXR-5	0.01
50	NIM-G	0.01
50?	MO8-1	0.01
49	KK	0.01
48	GS-N	0.01
46	DTS-1	0.01
45	BCS-395	0.01
45	G-1	0.01
44	GSD-2	0.01
44	GSD-8	0.01
44?	M-3	0.01
43?	GL-O	0.01
41	PCC-1	0.01
40	JG-1	
39?	GM	
36	RGM-1	
28?	DT-N	
24?	FK-N	
24?	NBS-69b	
20	AN-G	
16?	I-1	
16?	NBS-696	
12	BCS-375	
12?	FK	
10?	NIM-S	
5	BCS-376	
1.4	IS-1	

Table 118. Zr contents, in descending order

Zr ppm	Sample	ZrO$_2$ pct	Zr ppm	Sample	ZrO$_2$ pct	Zr ppm	Sample	ZrO$_2$ pct
	NIM-L	1.49	240	SGD-1A	0.03	140	GXR-5	0.02
1300	STM-1	0.18?	240?	GS-N	0.03	135	SCo-1	0.02
800?	Mica-Fe	0.11	240?	SdL-1	0.03	130	MAG-1	0.02
790?	SO-2	0.11	230	AGV-1	0.03	130	ST-1A	0.02
720	NS-1	0.10	220	GSD-3	0.03	125	DR-N	0.02
720	SG-1A	0.10	220	GSD-5	0.03	110?	JG-1	0.01
700?	VS-N	0.09?	220?	SOIL-5	0.03	105	GXR-6	0.01
520?	BX-N	0.07	210	G-1	0.03	105	MRG-1	0.01
500	GSP-1	0.07	200	GXR-2	0.03	105	W-1	0.01
490	GSD-8	0.07	200	GXR-4	0.03	100?	M-2	0.01
470?	NBS-97a	0.06	200	RGM-1	0.03	100?	W-2	0.01
460	GSD-2	0.06	200?	BCS-375	0.03	98	BM	0.01
400	ASK-1	0.05	190	GSD-4	0.03	81?	SO-1	0.01
370?	DT-N	0.05	190	I-3	0.03	70	NBS-91	0.01
320	SY-3	0.04	185	BCR-1	0.02	70?	FK	0.01
310	GSD-1	0.04	180	BHVO-1	0.02	70?	GnA	0.01
310?	NBS-1633	0.04	180	GR	0.02	66	GXR-1	0.01
310?	NBS-98a	0.04	180	TB	0.02	60?	I-1	0.01
310?	SO-4	0.04	175	QLO-1	0.02	55?	SGR-1	0.01
300	G-2	0.04	170	ASK-2	0.02	44?	NBS-165a	0.01
300	NIM-G	0.04	170	GSD-6	0.02	38?	DNC-1	0.01
300?	SDC-1	0.04	165	GSD-7	0.02	33?	NIM-S	
290?	M-3	0.04	155	JB-1	0.02	30?	NIM-P	
280	SY-2	0.04	150	GA	0.02	27?	MA-N	
280?	TS	0.04	150	GH	0.02	23?	NIM-N	
270	BE-N	0.04	150	GM	0.02	20?	Mica-Mg	
250	BR	0.03	150?	SO-3	0.02	18?	BIR-1	
250	NBS-81a	0.03	150?	T-1	0.02	15	AN-G	
						8?	UB-N	

CONCLUSION

This report was written with three main goals in mind: to review developments in the general field of reference samples for the analysis of geological materials (mainly rocks), to summarize the contributions to that work provided by the laboratories of the Analytical Chemistry Section of the Geological Survey of Canada, and to provide detailed information on available samples at the time of writing.

There can be little controversy concerning the first goal, other than the age-old question of what should or should not have been included.

The second goal may be itself resolved into three subcategories: i.e. our contributions to collaborative analytical programs originating in other institutions, similar programs co-ordinated or originated here, and this writer's development of the "select laboratories method". Our contributions to other programs are mentioned in the notes describing the various samples. It may be noted with some satisfaction that whenever the select laboratories method was applied to programs to which we had contributed, at least our chemical and x-ray laboratories have always been among the select group. Only two programs were centred on our laboratories – that on SY-2, SY-3 and MRG-1, and the current work (at this writing) on the four iron-formation rocks. The former group of samples has found world-wide acceptance. Fortunately, a good supply of additional material remains on hand for all three. The work on the iron-formation rocks may not be completed for some time to come, although a fair number of results have begun to arrive.

As in the main body of the report, the subject of the select laboratories method must receive special attention in this Conclusion. The rationale behind the scheme has been explained in the text, but it must be admitted that no other compiler of data has adapted this highly pragmatic approach to the resolution of disparate data. Statistically-oriented critics have disparaged the method because of its lack of rigour. Still, none has been able to refute the claims of validity on the basis of the summation, iron-oxide compatibility and comparative analytical tests. The three tests are known to be of limited value, but no one has suggested anything better. Those who have concentrated on rigorous statistical schemes (which occasionally contradict one another) have merely been satisfied to point out that their derived values lie "close to" others. On the other hand, it is gratifying to note that some other compilers, who base their initial computations on orthodox statistical ideas, have made their final decisions as a result of some subjective considerations. Even in those cases, it is shown in this report that some of the resulting values can be seriously challenged by values derived by the select laboratories method.

Finally, the information on currently available reference materials, which accounts for the major portion of the entire report, is what will likely prove of maximum usefulness to other workers in "geoanalysis". Parts II and III of the paper represent the author's sixth attempt at providing reasonably comprehensive coverage and critical comment on the increasingly large number of available samples. The references list a number of examples of similar work done by others, but none of them can claim as great a coverage, as useful means of presentation, or perhaps most important of all, as meaningful discussion of the backgrounds and merits of particular samples.

Over the last 13 years, this writer has devoted an increasing proportion of his time to the subject with which this report is concerned. Has it been worth the effort? Only the reaction of widely recognized authorities in the field can provide the answer. Up to the present, such reactions have been encouraging, if not always favourable.

ACKNOWLEDGMENTS

In reviewing material covering so long a period of time, based on information garnered from so many sources, it becomes difficult to recall the many people whose co-operation has made it all possible. Apologies are therefore offered in advance to any who are overlooked. Such omissions must be blamed on failing memory rather than on ingratitude.

Thanks are due to the co-ordinators of the various reference samples, originating in so many different institutions and to contributors of data on our own samples. Some have been more helpful than others, but one stands head and shoulders above the rest. The name of K. Govindaraju, of CRPG, France, has been singled out in the text on several occasions, in recognition of his massive contributions. Not the least of these have been his indefatigable labours on the Geostandards Newsletter. The large number of references to papers in that publication bear witness to the great importance of that work – on a journal which is not yet six years old!

T.W. Steele, of the National Institute for Metallurgy, South Africa, deserves special recognition, in particular for his incisive but generally constructive criticism of this author's work, for providing him with information before publication and for making the valuable suggestion that a distinction be made, in the listings in this publication, between usable values originating with suppliers of particular samples, and usable values derived by the select laboratories method.

F.J. Flanagan, of the U.S. Geological Survey, casually called "Father", has earned that title in a more literal sense. He has been involved in the subject for as long a time as (or longer than) almost anyone. Much as we may have disagreed (informally as well as in the literature), no one can deny his part in the promotion of the subject. He has been more than generous in providing us with samples (without charge) as well as with numerical values and other background information.

Many others must be remembered for a variety of contributions, e.g. (in-more-or-less random order): Mme L. Savoyant, Université des Sciences et Techniques de Languedoc (France) and W.M. Johnson, British Columbia Ministry of Mines and Petroleum Resources, for the particularly high quality of their data on SY-2, SY-3 and MRG-1; Z. Sulcek and I. Rubeska, Central Geological Institute (Czechoslovakia), for the invitation to address the INTERAN Conference, Prague, 1976, on the subject of reference materials; Z. Valcha and J. Dempir, Institute of Mineral Raw Materials (Czechoslovakia), for providing information on samples produced in Eastern Europe, on methods used in resolving disparate data, and for providing a generous supply of the samples themselves; R. Dybczynski, Institute of Nuclear Research (Poland), and O.H.J. Christie, Rogaland District High School (Norway), for providing copies of their computer programs used in resolving data; R. Schindler, Zentrales Geologisches Institut (East Germany) for generous supply of their samples and valuable exchange of ideas; A. Colombo, EURATOM, Italy, for advance information on material intended for publication; A. Ando, Geological Survey of Japan; E.S. Gladney, Los Alamos Scientific Laboratory (USA); C.O. Ingamells, AMAX Corp. (USA); B.J. Lister, Institute of Geological Sciences (U.K.); M. Sankar Das, Bhabha Atomic Research Centre (India); G. Jecko, Institut de Recherches de la Sidérurgie (France); E.S. Pilkington, CSIRO (Australia) and S.V. Lontsikh, Vinogradov Institute of Geochemistry (USSR); all for valuable and stimulating exchanges of ideas (not always in accord!).

Closer to home, this writer is indebted to Guy Perrault, Ecole Polytechnique, and A.H.C.P. Gillieson, CANMET (retired) for initiating the work on MRG-1, SY-2 and SY-3; as well as to H.F. Steger, R. Sutarno and G.H. Faye (retired), all of CCRMP, for their co-operation in preparing samples, treating data and general exchange of ideas.

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Yang Jun-hao, of the Uranium Geology Institute (China), as a visiting scientist at the Geological Survey of Canada, has provided valuable assistance in several phases of the computer work mentioned in the preceding paragraph.

Above all, mention must be made of the support and encouragement provided by J.A. Maxwell, Director, Central Laboratories and Technical Services Division, GSC, at all stages of our work in reference materials and for critical reading of the manuscript.

LATE DEVELOPMENTS

Preparation of the manuscript for this paper was done over a period of about 18 months. A number of developments that occurred during that period have been embodied in the main body of the report – as revealed by tables numbered 11a and 40a. The following notes concern developments that followed completion of the main manuscript, and may be of interest to readers:

1) The Geological Survey of Japan has produced a proposed reference sample of rhyolite, JR-1, and is now soliciting analytical data on it, as well as on JA-1 and JB-2 (see Table 42).

2) A paper by Graham et al. (1982) appeared in Analytical Chemistry, v. 54, p. 1623-1627, entitled "Determination of elements in NBS geological standard reference materials by neutron activation analysis". The data in that paper could lead to the derivation of additional usable values for samples NBS-278 and -688.

3) Through the courtesy of Ma Guang-zu, of the Institute of Analytical Techniques of the Chinese Academy of Geological Sciences, the Geological Survey of Canada has been provided with four new reference samples, chromites DZCr-1 and DZCr-2, and ultrabasic rocks DZΣ-1 and DZΣ-2. The samples originated with the Xian Institute of Geology and Mineral Resources of the Chinese Academy of Geological Sciences, who also provided an English translation of their "Explanatory Note on the Reference Materials of the Chromite and the Ultrabasic Rocks". That note included a listing of individual results reported by 17 Chinese laboratories, information on methods used, and a set of "standard values".

   Unlike the collaborative analysis involved in most of the other reference materials described in this report, the individual results show a highly satisfactory degree of consistency. For example, silica results at the 34 to 38 per cent level have a standard deviation of only 0.12 to 0.13. Even ferrous iron, for which the listed values are given as "provisional", shows standard deviations of only 0.08 to 0.11 over the 2 to 13 per cent concentration range. In view of the excellent coherence of the individual results, there can be no hesitation in accepting their arithmetic averages as usable values.

   Other aspects of the information on these samples are somewhat puzzling. The listing of "analytical methods" used by individual laboratories for each constituent suffers from the common shortcoming of showing merely techniques of measurement, with no indication of sample pre-treatment. "Standard values" for all six metals of the platinum group are given for all four samples, a highly useful set of information which is sadly lacking from most other rock reference materials. However, the values shown are of essentially the same order of magnitude for all six metals in each sample, where relatively higher concentrations of platinum would normally be expected. Further, the summations are very close to 100 per cent, a condition seldom attained with ultrabasic rocks because of the possible presence of some elements (notably nickel) in the metallic state.

   Nevertheless, these samples are a welcome addition to the limited number of available reference samples of ultrabasic rocks. In Table 120, the letters XIGMR are the initials of the originating institute; the usable values for the two rocks are presented in much the same way as those for other samples in this report. (The information was unfortunately received too late for embodiment in the concentration ladders of Part III.) There is a slight difference between Table 120 and the data provided by the originators. In the former case, summations were corrected as "oxygen for chlorine and sulphur"; the latter case did not involve a sulphur correction.

4) Shortly after the completion of this manuscript, word was received of the death of T.W. Steele. An indefatigable innovator in both "geoanalysis" and "geostandards", as well as in similar metallurgical applications, Trevor Steele will be sadly missed by his many friends and colleagues throughout the world.

REFERENCES

Abbey, S.

1970: U.S. Geological Survey standards – A critical study of published analytical data; Canadian Spectroscopy, v. 15, p. 10-16.

1972: "Standard samples" of silicate rocks and minerals – A review and compilation; Geological Survey of Canada, Paper 72-30.

1973: Studies in "standard samples" of silicate rocks and minerals. Part 3: 1973 extension and revision of "usable" values; Geological Survey of Canada, Paper 73-36.

1975a: Critical comment – 1972 values for geochemical reference samples; Geochimica et Cosmochimica Acta, v. 39, p. 535-537.

1975b: Studies in "standard samples" of silicate rocks and minerals. Part 4: 1974 edition of "usable" values; Geological Survey of Canada, Paper 74-41.

1977a: "Standard Samples": How "standard" are they?; Geostandards Newsletter, v. 1, p. 39-45.

1977b: Studies in "standard" samples for use in the general analysis of silicate rocks and minerals. Part 5: 1977 edition of "usable" values; Geological Survey of Canada, Paper 77-34. (See also X-ray Spectrometry (1978), v. 7, p. 99-121.)

Abbey, S. (cont.)

1977c: Topics on "Geostandards" during the INTERAN '76 Conference on Analysis of Geological Materials; Geostandards Newsletter, v. 1, p. 5-6.

1978: U.S.G.S. II revisited; Geostandards Newsletter, v. 2, p. 141-146.

1979: Reference materials – Rock samples SY-2, SY-3, MRG-1; CANMET Report 79-35.

1980: Studies in "standard samples" for use in the general analysis of silicate rocks and minerals. Part 6: 1979 edition of "usable" values; Geological Survey of Canada, Paper 80-14. (See also Geostandards Newsletter (1981), v. 4, p. 163-190; Johnson and Maxwell (1981), p. 407-464)

1981a: The search for "best values" – A study of three Canadian rocks; Geostandards Newsletter, v. 5, p. 13-26.

1981b: Reliability in the analysis of rocks and minerals; Analytical Chemistry, v. 53, p. 528A-534A.

1982a: An evaluation of USGS III; Geostandards Newsletter, v. 6, p. 47-76.

1982b: Exchange of comments on "Matrix interferences in graphite furnace atomic absorption spectrometry by capacitive discharge heating"; Analytical Chemistry, v. 54, p. 136-137.

Abbey, S., and Govindaraju, K.

1978: Analytical data on three rock reference samples from the Institute of Geochemistry, Irkutsk, U.S.S.R.; Geostandards Newsletter, v. 2, p. 15-22.

Abbey, S., Meeds, R.A., and Bélanger, P.G.

1979: Reference samples of rocks – The search for "best values"; Geostandards Newsletter, v. 3. p. 121-133

Andersson, L.-H., and Christie, O.H.J.

1975: Progress Report 1967-1975; Analytisk Spor-element Komité Norden, Oslo.

Ando, Atsushi

1967: Announcement: A new silicate rock standard, JG-1 issued from the Geological Survey of Japan; Geochemical Journal, v. 1, p. 155

1968: Announcement: A new silicate rock standard, JB-1 issued from the Geological Survey of Japan; Geochemical Journal, v. 2, p. 185

Ando, Atsushi; Kurasawa, Hajime; Ohmori, Teiko; and Takeda, Eizo

1971: 1971 compilation of data on rock standards JG-1 and JB-1 issued from the Geological Survey of Japan; Geochemical Journal, v. 5, p. 151-164.

1974: 1974 compilation of data on the GSJ geochemical reference samples JG-1 granodiorite and JB-1 basalt; Geochemical Journal, v. 8, p. 175-192

Ando, Atsushi; Kurasawa, Hajime; and Uchiumi, Shigeru

1975: Evaluation of Rb, Sr, K and Na contents of GSJ JG-1 granodiorite and JB-1 basalt; Bulletin Geological Survey of Japan, v. 26, p. 27 (335)-30(348).

Andrews, D.F., Bickel, P.J., Hampel, F.R., Huber, P.J., Rogers, W.H., and Tukey, J.W.

1972: Robust estimates of location survey and advances; Princeton University Press

Anonymous

1961: Report of the Nonmetallic Standards Committee, Canadian Association for Applied Spectroscopy; Applied Spectroscopy, v. 15, p. 159-161

Belyaev, Yu. I., and Sobornov, O.P.

1981: Uranium, thorium and potassium in reference samples; Geostandards Newsletter, v. 5, p. 109-111

Benedetti, A, Frache, R, Jaffrezic, H, Joron, J.L., Mazucotelli, A., Meloni, S, and Oddone, M.

1977: Major, minor and trace element data of ophiolite standard rock GOG-1; Ofioliti, v. 2, p. 29-39.

Berman, S.S.

1981: Marine sediment reference materials, trace metals and inorganic constituents; Geostandards Newsletter, v. 5, p. 218

Bowden, P., and Luena, G.

1966: The use of T-1 as a geochemical standard; Geochimica et Cosmochimica Acta, v. 30, p. 361.

Bowman, W.S., Faye, G.H., Sutarno, R., McKeague, J.A., and Kodama, H.

1979: Soil samples SO-1, SO-2, SO-3 and SO-4 – Certified reference materials; CANMET Report 79-3.

British Ceramic Research Association

1979: Announcement; Geostandards Newsletter, v. 3,. p. 209

Brunfelt, A.O., and Steinnes, E.

1966: Instrumental neutron-activation analysis of "standard rocks"; Geochimica et Cosmochimica Acta, v. 30, p. 921-928.

1978: Neutron activation analysis for trace element determination trace element determination in geostandards; Geostandards Newsletter, v. 2, p. 3-7.

Bureau of Analysed Samples Ltd.

1979: BAS Certified Reference Materials; Bureau of Analysed Samples Ltd., Catalogue No. 477

1981: Supplementary information regarding trace element content [on BCS feldspars, magnesite, dolomite and bauxite]; Announcement, Bureau of Analysed Samples Ltd., September.

Burgess, G.K.

1931: Bureau of Standards Certificate of Analysis of Standard Sample No. 91 – Opal Glass, National Bureau of Standards.

Burks, H.G., and Palliser, J.W.

1961: Standard geochemical sample T-1, Msusulu tonalite; Government Printer, Dar-es-Salaam.

Cali, J.P.

1969a: National Bureau of Standards Certificate – Standard Reference Material 97a, Flint Clay

1969b: National Bureau of Standards Certificate – Standard Reference Material 98a, Plastic Clay

1975: National Bureau of Standards Certificate – Standard Reference Material 1633, Trace Elements in Coal Fly Ash

1978a: National Bureau of Standards Certificate – Standard Reference Material 81a, Glass Sand

1978b: National Bureau of Standards Certificate – Standard Reference Material 165a, Glass Sand

1978c: National Bureau of Standards Certificate – Standard Reference Material 1645, River Sediment

Chakrabarti, C.L., Wan, C.C., Hamed, H.A., and Bertels, P.C.

1981: Matrix interferences in graphite furnace atomic absorption spectrometry by capacitive discharge heating; Analytical Chemistry, v. 53, p. 444-450

1982: Reply to comment (Abbey, 1982b); Analytical Chemistry, v. 54, p. 137-138.

Chayes, F.

1969: A last look at G-1-W-1; Carnegie Institution of Washington Year book 67, 1967-68, p. 239-241

1970. Another last look at G-1-W-1; International Association of Mathematical Geology Journal, v. 2, p. 207-209.

Christie, O.H.J.

1975: Three trace-element geological materials certified as a result of a co-operative investigation; Talanta, v. 22, p. 1048-1050.

Christie, O.H.J., and Alfsen, K.H.

1977: Data transformation as a means to obtain reliable consensus values for reference materials; Geostandards Newsletter, v. 1, p. 47-49

Colombo, A.

1980a: The Gamma transformation mode: A mode or a median?; Geostandards Newsletter, v. 4, p. 199-203.

1980b: Another approach to the mode of a skewed set of data: the plot method; Geostandards Newsletter, v. 4, p. 239-242

Date, A.R.

1978: Preparation of trace element reference materials by a co-precipitated Gel Technique; Analyst, v. 103, p. 84-92

1982: Geological reference materials with particular emphasis on multi-element trace analysis; Analytical Proceedings, v. 19, p. 7-12.

de la Roche, H., et Govindaraju, K.

1969: Rapport sur deux roches, diorite DR-N et serpentine UB-N, proposées comme étalons analytiques par un groupe de laboratoires français; Bulletin de la Société Française de la Céramique, n° 85, p. 35-50

1971: Rapport sur un minerai d'aluminium bauxite BX-N et sur réfractaire silico-alumineax disthène DT-N proposés comme étalons analytiques; Bulletin de la Société Française de la Céramique, n° 90, p. 3-19.

1973a: Rapport (1972) sur quatre standards géochimiques de l'Association Nationale de la Recherche Technique: diorite DR-N, serpentine UB-N, bauxite BX-N et disthène DT-N; Bulletin de la Société Française de la Céramique, n° 100, p. 49-75.

1973b: Étude coopérative sur un verre synthétique VS-N proposé comme étalon analytique pour le dosage des éléments en traces dans les silicates; Analusis (Paris), v. 2, p. 59-70.

1975: Glass calibration standards for trace element analysis; Report to Group 35 A "Etalons analytiques de minéraux, minerais et roches", Association nationale de la recherche technique, 23 Mai.

1976: Nouveau étalons géochimiques granite GS-N et feldspath FK-N; Analusis (Paris), v. 4, p. 347-372.

1982: AL-I and IF-G; Geostandards Newsletter, v. 6, p. 173

de la Roche, H., Govindaraju, K., et Odin, G.S.

1976: Préparation d'un étalon analytique de glauconite; Analusis (Paris), v. 4, p. 385-397

Dempir, J.

1978: Preparation of reference samples of mineral raw materials and their use in analytical practice; Geostandards Newsletter, v. 2, p. 117-120.

Dixon, W.J.

1953: Processing data for outliers; Biometrics, v. 9, p. 74-89

Dixon, W.J., and Massey, F.J.

1957: Introduction to Mathematical Statistical Analysis; McGraw-Hill

Dybczynski, R.

1980: Comparison of the effectiveness of various procedures for the rejection of outlying results and assigning consensus values in interlaboratory programs involving determination of trace elements or radionuclides; Analytica Chimica Acta, v. 117, p. 53-70.

Dybczynski, R., Tugsavil, A., and Suschny, O.

1979: Soil-5, A New IAEA Certified Reference Material for Trace Element Determinations; Geostandards Newsletter, v. 3, p. 61-87

Ellis, P.J., Copelowitz, I, and Steele, T.W.

1977: Estimation of the mode by the dominant cluster method; Geostandards Newsletter, v. 1, p. 123-130.

Fairbairn, H.W., (ed.) and others

1951: A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks; United States Geological Survey Bulletin 980.

Fairbairn, H.W., and Schairer, J.F.

1952: A test of accuracy of chemical analysis of silicate rocks; American Mineralogist, v. 37, p. 744-757.

Ferguson, T.S.

1961a: Rules for the rejection of outliers; Review of the Institute of International Statistics v. 3, p. 29-43

1961b: On the rejection of outliers; Fourth Berkeley Symposium on Mathematical Statistics and Probability; University of California Press

Flanagan, F.J.

1967: U.S. Geological Survey silicate rock standards; Geochimica et Cosmochimica Acta, v. 31, p. 289-308

1969: U.S. Geological Survey standards – II. First compilation of data for the new U.S.G.S. rocks; Geochimica et Cosmochimica Acta, v. 33, p. 81-120.

1970: Sources of geochemical standards – II; Geochimica et Cosmochimica Acta, v. 34, p. 121-125.

1973: 1972 values for international geochemical reference samples; Geochimica et Cosmochimica Acta, v. 37, p. 1189-1200.

1975: Author's reply (to Critical comment – 1972 values for geochemical reference samples); Geochimica et Cosmochimica Acta, v. 39. p. 537-540.

Flanagan, F.J. (ed.)

1976a: Description and analyses of eight new USGS rock standards; United States Geological Survey, Professional Paper 840.

Flanagan, F.J.

1976b: G-1 et W-1: Requiescant in pace!; United States Geological Survey, Professional Paper 840, p. 189-192.

1976c: 1972 compilation of data on USGS standards; United States Geological Survey, Professional Paper 840, p. 131-183

Flanagan, F.J., and Carroll, G.V.

1976: Mica schist, SDC-1, from Rock Creek Park, Washington, D.C.; United States Geological Survey, Professional Paper 840, p. 29-32

Flanagan, F.J., and Gottfried, D.

1978: Standards for low level trace element abundances; [Circular letter, United States Geological Survey, to] Recipients [of samples BIR-1, DNC-1, W-2], June 21.

1980: USGS Rock Standards, III: Manganese-nodule reference samples USGS-NOD-A-1 and USGS-NOD-P-1; United States Geological Survey, Professional Paper 1155

Flanagan, F.J., and Gwyn, M.E.

1967: Sources of geochemical standards; Geochimica et Cosmochimica Acta, v. 31, p. 1211-1213.

Flanagan, F.J., Wright, T.L., Taylor, S.R., Annell, C.S., Christian, R.C., and Dinnin, J.I.

1976: Basalt, BHVO-1, from Kilauea Crater, Hawaii; United States Geological Survey, Professional Paper 840, p. 33-39

Fleischer, M.

1965: Summary of new data on rock samples G-1 and W-1, 1962-1965; Geochimica et Cosmochimica Acta, v. 29, p. 1263-1284

1969: U.S. Geological Survey standards – I. Additional data on rocks G-1 and W-1, 1965-1967; Geochimica et Cosmochimica Acta, v. 33, p. 65-69

Fleischer, M., and Stevens, R.E.

1962: Summary of new data on rock samples G-1 and W-1; Geochimica et Cosmochimica Acta. v. 26, p. 525-543

Frick, C.

undated: The occurrence and petrography of the SAROCK standards; Geological Survey of South Africa Report.

Friese, G., and Grassmann, H.

1967: Die Standardgesteinsproben des ZGI – 4. Mitteilung: Diskussion der Gehalte an einigen Hauptkomponenten auf Grund neuer Analysen; Zeitschrift für angewandte Geologie, v. 13, p. 473-477

Geary, R.C.

1935: The ratio of the mean deviation to the standard deviation as a test of normality; Biometrika, v. 27, p. 310-322

1936: Moments of the ratio of the mean deviation to the standard deviation for normal supplies; Biometrika, v. 28, p. 295-307

Gladney, E.S.

1980: Compilation of elemental concentration data for NBS biological and environmental standard reference materials; Analytica Chimica Acta, v. 118, p. 385-396; also in LA-8438-MS, Informal Report, Los Alamos Scientific Laboratory, 1980 07.

Gladney, E.S. (cont.)

1981: Comparison of methods for calculation of recommended elemental concentrations for Canadian Certified Reference Materials Project rock standards SY-2, SY-3 and MRG-1; Los Alamos Scientific Laboratory Report LA-8770-MS

Gladney, E.S., and Goode, W.E.

1981: Elemental concentrations of eight new United States Geological Survey rock standards: a review; Geostandards Newsletter, v. 5, p. 31-64

Gladney, E.S., Perrin, D.R., Owens, J.W., and Knab, D.

1979: Elemental concentrations in the United States Geological Survey's Geochemical Exploration reference samples – A review; Analytical Chemistry, v. 51, p. 1557-1569.

Govindaraju, K.

1979: Report (1968-1978) on two mica reference samples: Biotite Mica-Fe and Phlogopite Mica-Mg; Geostandards Newsletter, v. 3, p. 3-24.

1980: Report (1980) on three GIT-IWG rock reference samples: anorthosite from Greenland, AN-G; basalte d'Essey-la-Côte, BE-N; granite de Beauvoir, MA-N; Geostandards Newsletter, v. 4, p. 49-138.

1982: Report (1967-1981) on four ANRT rock reference samples: Diorite DR-N, Serpentine UB-N, Bauxite BX-N and Disthene DT-N; Geostandards Newsletter, v. 6, p. 91-159.

Govindaraju, K., et de la Roche, H.

1977: Rapport (1966-1976) sur les éléments en traces dans trois roches standards géochimiques du CRPG: Basalte BR et Granites GA et GH; Geostandards Newsletter, v. 1, p. 67-100

Grassmann, H.

1964: Die Standardgesteinsprobem des ZGI – 1. Mitteilung; Zeitschrift für angewandte Geologie, v. 10, p. 555-557

1966: Die Standardgesteinsproben des ZGI – 3. Mitteilung: Ergebnisse der chemischen Analysierung auf hauptkomponenten; Zeitschrift fur angewandte Geologie, v. 12, p. 368-378

1972: Die Standardgesteinsproben des ZGI. 6 Mitteilung: Neue Auswertung der Analysen auf Hauptkomponenten der Proben Granit GM, Basalt BM, Tonschiefer TB, Kalkstein KH und erste Auswertung der Proben Anhydrit AN und Schwarzschiefer TS; Zeitschrift fur angewandte Geologie, v. 18, p. 280-284.

Grubbs, F.E.

1950: Sample criteria for testing outlying observations; Annals of Mathematical Statistics, v. 21, p. 27-58.

1969: Procedures for detecting outlying observations in samples; Technometrics, v. 2, p. 1-21.

Harris, J.L., Schwarz, L.J., d'Angelo, W.M., and Flanagan, F.J.

1981: Additional analytical data for gabbro, GOG-1; Geostandards Newsletter, v. 5, p. 125-128.

Ingamells, C.O.

1978: Standard reference materials in geoexploration and extractive metallurgy research; Geoanalysis '78 Symposium, Ottawa, May.

International Atomic Energy Agency (IAEA)

1978: Information Sheet: Certified Reference Material, Soil-5, 5 Oct.; International Atomic Energy Authority, Vienna

1979: Information Sheet: Certified Reference material, SL-1 15 Dec.; International Atomic Energy Authority, Vienna

1982: Information Sheet [on Analytical Quality Control Services]; International Atomic Energy Agency, Vienna.

Ivanov, E.A.

1981: Rapport preliminaire sur un échantillon géochimique de Bulgarie: Granite G-B; Geostandards Newsletter, v. 5, p. 27-29

Iwata, Yasuo; Matsumoto, Kazuko; Haraguchi, Hiroki; Fuwa, Keiichiro; and Okamoto, Kensaku

1981: Proposed certified reference material for pond sediment; Analytical Chemistry, v. 53, p. 1136-1138

Jecko, G.

undated: Échantillon-type de laitier de haut fourneau LO1-1 – Certificat d'Analyse; Institut de Recherches de la Sidérurgie.

1970: Échantillon-type de marne ferrifère M08-1 – Certificat d'Analyse; Institut de Recherches de la Sidérurgie.

Jeffery, P.G., and Hutchison, D.

1981: Chemical Methods of Rock Analysis; 3rd edition, Pergamon, p. 5-8

Johansen, O., and Steinnes, E.

1966: Determination of indium in standard rocks by neutron activation analysis; Talanta, v. 13, p. 1177-1181

Johnson, W.M., and Maxwell, J.A.

1981: Rock and Mineral Analysis; 2nd edition, Wiley.

Kato, Yuzo; Onuki, Hitoshi; and Aoki, Ken-ichiro

1978: Major element analyses on the geochemical standards JA-1 and JB-2; Journal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists, v. 73, p. 281-282

Kennedy, P.C., Palmer, K., and Roser, B.P.

1981: Chemical analysis of the eight U.S.G.S. rock standards BHVO-1, MAG-1, QLO-1, RGM-1, SCo-1, SDC-1, SGR-1, STM-1; Publications of the Geology Department, Victoria University of Wellington, New Zealand, No. 21

Knechtel, J.R., and Fraser, J.L.

1980: Sludge ash reference sample; Geostandards Newsletter, v. 4, p. 213-215

Kukharenko, A.A. et multi alia

1968: Clarke values of the Khibinsky alkaline massif; Vsesoyuznoye Mineralogicheskoye Obshschestvo, Zapiski [All-Union Mineralogical Society, Reports], v. 97 (pt. 2) p. 133-149 (in Russian).

Larsen, E.S.

1938: The accuracy of chemical analyses of amphiboles and other silicates; American Journal of Science (5), v. 35, p. 94-103

Lehmden, D.J. (von); Jungers, R.H.; and Lee, R.E., Jr.

1974: Determination of trace elements in coal, fly ash, fuel oil and gasoline – A preliminary comparison of selected analytical techniques; Analytical Chemistry, v. 46, p. 239-245

Lontsikh, S.V., and Parshin, A.K.

1979: Standard reference samples of rocks, soils, rare metal ores and concentrates; Zhurnal Analiticheskoy Khimii, v. 34, p. 2446-2452 (in Russian)

Lontsikh, S.V., Sidorovski, A.I., and Zakovyrin, O.M.

1979: On the chemical composition of standard reference samples of rocks ST-1A, SGD-1A and SG-1A; Zhurnal Analiticheskoy Khimii, v. 34, p. 2453-2456 (in Russian).

Lundell, G.E.F.

1933a: The chemical analysis of things as they are; Industrial and Engineering Chemistry, Analytical Edition, v. 5, p. 221-225.

1933b: Chemical analysis of glass; Industrial and Engineering Chemistry, v. 25, p. 853-856.

Manheim, F.T., Hathaway, J.C., Flanagan, F.J., and Fletcher, J.D.

1976: Marine mud, MAG-1 from the Gulf of Maine; United States Geological Survey Professional Paper 840, p. 25-28

Mason, G.L., and Bowman, W.S.

1977: Blast furnace slag SL-1: Its preparation for use as a certified reference material; CANMET Report 77-57.

McLeod, C.R., Wan Liang-guo, and Abbey, S.

1982: Mineralogy and petrology of four "standard" samples of iron formation; in Current Research, Part A, Geological Survey of Canada, Paper 82-1A, p. 435-437

Meinke, W. W.

1965a: National Bureau of Standards Certificate – Standard Reference Material 70a, Feldspar (Provisional)

1965b: National Bureau of Standards Certificate – Standard Reference Material 99a, Feldspar (Provisional)

Moore, D.M.

1978: A sample of the Purington Shale prepared as a geochemical standard; Journal of Sedimentary Petrology, v. 48, p. 995-998

Morrison, G.H.

1975: General aspects of trace analytical methods. I. Methods of calibration in trace analysis; Pure and Applied Chemistry, v. 41, p. 397-403

1980: Analytical Controversies; Analytical Chemistry, v. 52, p. 1793

Myers, A.T., Havens, R.G., Connar, J.J., Conklin, N.M., and Rose, H.J.Jr.

1976: Glass reference standards for the trace-element analysis of geological materials – Compilation of interlaboratory data; United States Geological Survey, Professional Paper 1013.

National Bureau of Standards (U.S.A.)

1979: NBS Standard Reference Materials Catalog, 1979-80 Edition; National Bureau of Standards, Special Publication 260

Neil, Sarah T.

1980: Chemical analysis of USGS manganese nodule reference samples; Geostandards Newsletter, v. 4, p. 205-212

Odin, G.S., et collaborateurs

1976: La glauconite GL-O, étalon inter-laboratoires pour l'analyse radiochronométrique; Analusis (Paris), v. 4, p. 287-291.

Ondov, J.M., Zoller, W.H., Olmez, I., Aras, N.K., Gordon, G.E., Rancitelli, L.A., Abel, K.H., Filby, R.H., Shah, K.R., and Ragaini, R.C.
1975: Elemental concentrations in the National Bureau of Standards' environmental coal and fly ash standard reference materials; Analytical Chemistry, v. 47. p. 1102-1109

Peck, L.C.
1964: Systematic analysis of silicates; United States Geological Survey, Bulletin 1170, p. 51-53, 82-83

Perrault, G., Hébert, P., et Kubat, V.
1974: MRG-1, un nouveau matériau de référence de gabbro à pyroxène et olivine du Mont-Royal, P.Q., Canada; Canadian Journal of Spectroscopy, v. 19, p. 63-67

Poole, A.B.
1972: A Third Report on the Standard Rocks QMC I1, QMC I3, QMC M2 and QMC M3; Queen Mary College, Department of Geology, University of London.

Reeves, R.D., and Brooks, R.R.
1978: Trace Element Analysis of Geological Materials, Wiley-Interscience, p. 81-89

Ridsdale, N.D.
1955: Certificate of analyses – B.C.S. No. 267, Silica Brick; British Chemical Standards issued by Bureau of Analysed Samples, Ltd.

Ridsdale, P.D.
1961: Certificate of Analyses – B.C.S. No. 309 Sillimanite; British Chemical Standards issued by Bureau of Analysed Samples, Ltd.

1965: Certificate of Analyses – B.C.S. No. 313 High Purity Silica (0.1% Alumina); British Chemical Standards issued by Bureau of Analysed Samples, Ltd.

1970a: Certificate of Analyses – B.C.S. No. 375 Soda Feldspar; British Chemical Standards issued by Bureau of Analysed Samples, Ltd.

1970b: Certificate of Analyses – B.C.S. No. 376 Potash Feldspar; British Chemical Standards issued by Bureau of Analysed Samples, Ltd.

1970c: Certificate of Analyses – B.C.S. No. 367 Blast Furnace Slag; British Chemical Standards issued by Bureau of Analysed Samples, Ltd.

1974: Certificate of Analyses – B.C.S. no. 302/1 Northamptonshire Iron ore; British Chemical Standards issued by Bureau of Analysed Samples, Ltd.

Roelandts, Iwan
1981: Weaknesses and strengths of geochemical reference materials; Chemical Geology, v. 32, p. 155-165

Roubault, M., de la Roche, H., et Govindaraju, K.
1964: L'analyse des roches silicatées par spectrométrie photo-électrique au Quantomètre A.R.L. et son contrôle par des roches étalons; Sciences de la Terre, v. 9, p. 339-371

1966: Report on four geochemical rock standards: Granites GR, GA, GH and Basalt BR; Sciences de la Terre, v. 11, p. 105-121

1968: Rapport (1966-1968) sur les standards géochimiques: granites GR, GA, GH; basalte BR; biotite ferrifère Mica-Fe; phlogopite Mica-Mg; Sciences de la Terre (Nancy), v. 4, p. 379-404.

Roubault, M., de la Roche, H., et Govindaraju, K. (cont.)
1970: Etat actuel (1970) des études co-opératives du Centre de Recherches Pétrographiques et Géochimiques; Sciences de la Terre, v. 15, p. 351-393.

Rubeska, Ivan
1977: The state of art of trace element analysis of geological samples as derived from results on standard rock samples; Geostandards Newsletter, v. 1, p. 15-20

Russell, B.G., Levin, J, Domel, G., Faure, P.K., Stoch, H, and Steele, T.W.
1968: Collection and preparation of standard rock samples; National Institute of Metallurgy, South Africa, Report no. 332

Russell, B.G., Goudvis, R.G., Domel, G., and Levin, J.
1972: Preliminary report on the analysis of the six NIMROC geochemical standard samples; National Institute of Metallurgy, South Africa, Report no. 1351

Sandell, E.B.; and Onishi, Hiroshi
1978: Photometric Determination of Traces of Metals – General Aspects (Fourth Edition of Part I of "Colorimetric Determination of Traces of Metals"), Wiley, p. 180-182

Sankar Das, M.
1979: Geometric means as probable values for compiled data on geochemical reference samples: Geostandards Newsletter, v. 3, p. 199-205

Schindler, R.
1966: Die Standardgesteinsproben des ZGI – 2. Mitteilung: Erste zusammenfassende Betrachtung der Spurenelementanalysierung der Standardgesteine des ZGI, Berlin, und Vergleich mit den amerikanischen Gesteinen G-1 und W-1; Zeitschrift für angewandte, Geologie, v. 12, p. 188-196

1972: Standardgesteinsproben des ZGI. 5 Mitteilung: Stand der spurenelementanalyse der Gesteine GM, TB, BM und KH; Zeitschrift fur angewandte angew Geologie, v. 18, p. 221-228

Schindler, Rolf, und Scheutzow, Rudi
1975: Entwicklung und Anwendung von Standard proben fur die Spurenelementanalyse mineralische Rohstoffe: Zeitschrifte für angewandte, Geologie, v. 21, p. 130-136

Schlecht, W.G.
1951: Co-operative investigation of precision and accuracy in chemical analysis of silicate rocks; Analytical Chemistry, v. 23, p. 1568-1571

Schmitt, B.F., Segebade, C., and Fusban, H.-U.
1980: Waste incineration ash – a versatile environmental reference material; Journal of Radioanalytical Chemistry, v. 60, p. 99-109

Schultz, L.G., Tourtelot, H.A., and Flanagan, F.J.
1976: Cody shale, SCo-1, from Natrona County, Wyoming; United States Geological Survey, Professional Paper 840, p. 21-23

Shakespeare, W.
1623: "The Merchant of Venice", The First Folio, Act 4, Scene 1

Sidorovski, A.I., Parshin, A.K., and Fadeyev, A.G.
1976: Standard samples of chemical composition of rocks, soils, rare-metal ores and concentrates; in Unification and Standardization of Methods of Analysis for the Chemical Composition of Materials, Moscow, p. 72-77 (in Russian)

Sine, N.M., Taylor, W.O., Webber, G.R., and Lewis, C.L.

1969: Third report of analytical data for CAAS sulphide ore and syenite rock standards; Geochmica et Cosmochimica Acta, v. 33, p. 121-131

Smet. T., and Roelandts, I.

1978: Radiochemical neutron activation trace element analysis of two USGS ultrabasic rock reference samples: peridotite PCC-1 and dunite DTS-1; Geostandards Newsletter, v. 2, p. 61-70

Snavely, P.D. Jr., MacLeod, N.S., Flanagan, F.J., Berman, S., Nieman, H.G., and Bastron, H.

1976: Nepheline syenite STM-1, from Table Mountain, Oregon; United States Geological Survey Professional Paper 840, p. 7-10

South African Bureau of Standards

undated: Certificate of Analysis [for SARM 1-6 inclusive (NIM-G, -S, -L, -N, -P, -D)]; South African Bureau of Standards.

South African Committee for Certified Reference Materials

1974: Announcement: Igneous rocks; Certificates [for SARM 1-6 inclusive (NIM-G, -S, -L, -N, -P, -D)]; South African Bureau of Standards, Pretoria.

1979: Catalogue of certified reference materials; South African Bureau of Standards, Pretoria

Steele, T.W.

1977a: Topics on reference materials during the International Symposium (1976) on Analytical Chemistry in the Exploration, Mining and Processing of Materials; Geostandards Newsletter, v. 1, p. 21-23

1977b: A guide to the reporting of analytical results relating to the certification of geological reference materials; Geostandards Newsletter, v. 1, p. 31-33

1982: Reference materials; American Laboratory, January, p. 112-115.

Steele, T.W., and Hansen, R.G.

1979: Analysis of the NIMROC reference samples for major elements; National Institute of Metallurgy, South Africa Report No. 2016. (see also Geostandards Newsletter, v. 3, p. 135-172)

Steele, T.W., Wilson, A., Goudvis, R., Ellis, P.J., and Radford, A.J.

1978: Analyses of the NIMROC reference samples for minor and trace elements; National Institute of Metallurgy, South Africa, Report No. 1945. (see also Geostandards Newsletter, v. 2, p. 71-106)

Steger, H.F.

1980: Certified reference materials; CANMET Report 80-6E

Steinnes, E.

1981: Reference materials for trace analysis by radioanalytical methods: U.S. Geological Survey rock standards; Pure and Applied Chemistry, v. 53, p. 903-908

Stevens, R.E., and others

1960: Second report on a co-operative investigation of the composition of two silicate rocks; United States Geological Survey, Bulletin 1113.

Stevens, R.E., and Niles, W.W.

1960: Chemical analysis of the granite and diabase; United States Geological Survey, Bulletin, 1113, p. 3-43

Sutarno, R., and Faye, G.H.

1975: A measurement for assessing certified reference ores and related materials; Talanta, v. 22, p. 676-681.

Tatlock, D.B., Flanagan, F.J., Bastron, H., Berman, S., and Sutton, A.L. Jr.

1976: Rhyolite RGM-1, from Glass Mountain, California; United States Geological Survey, Professional Paper 840, p. 11-14

Tauson, L.V., Lontsikh, S.V., Shafrinsky, B.D., Kozlov, B.D. and Kochetkova, L.F.

1974: Geochemical standards of igneous rocks; Yezhegodnik 1974g, p. 370-375 (Institute of Geochemistry, Irkutsk) (in Russian)

Taylor, S.R., and Kolbe, P.

1964: Geochemical standards; Geochimica et Cosmochimica Acta, v. 28, p. 447-454.

Thomas, W.K.L., and Kempe, D.R.C.

1963: Standard geochemical sample T-1, Msusulu tonalite, Supplement No. 1; Government Printer, Dar-es-Salaam.

Uitterdijk Appel, P.W.

1980: Need for an iron-formation reference sample; Geostandards Newsletter, v. 4, p. 19.

Uriano, G.A.

1981a: National Bureau of Standards Certificate – Standard Reference Material 278, Obsidian Rock

1981b: National Bureau of Standards Certificate: Standard Reference Material 688, Basalt Rock.

Valcha, Z.

1969: A preliminary report on the preparation of magnesite and glass sand standards; Institute of Mineral Raw Materials, Kutna Hora (18 July)

1972: Standard reference sample of glass sand/Strelec. CSSR – "Guaranteed Values" and "Trace elements"; Institute of Mineral Raw Materials, Kutna Hora.

Vistelius, A.B.

1970: Statistical model of silicate analysis and results of investigation of G-1 and W-1 samples; International Association of Mathematical Geology Journal, v. 2, p. 1-14.

1971: Some lessons of the G-1-W-1 investigation; International Association of Mathematical Geology Journal, v. 3, p. 323-326.

Walker, G.W., Flanagan, F.J., Sutton, A.L. Jr., Bastron, H., Berman, S., Dinnin, J.I, and Jenkins, L.B.

1976: Quartz latite (dellenite) QLO-1, from southeastern Oregon; United States Geological Survey, Professional Paper 840, p. 15-20

Webber, G.R.

1965: Second report of analytical data for CAAS syenite and sulphide standards; Geochimica et Cosmochimica Acta, v. 29, p. 229-248

Yang Min-cai, Xie Xue-jin, Li Lian-zhong and Shen Wei-jun.

1981: A first set of usable values for eight GSD standard samples (Geochemical water system sediment); Report of the Institute of Geophysical Exploration, Beijing, September 1981. (In Chinese)

Zentrales Geologisches Institut

undated: Standard-Gesteinsproben; advertising brochure, Zentrales Geologisches Institut (East Berlin)

1973: Feldspatsand ZGI-FK, Mittelwerte aus 13 Laboratorien (Trockensubstanz); Auswertung Marz 1973.

Zentrales Geologisches Institut (cont.)

1975a: Geologische Industrie – Gesteins-Standardproben – Chemische Zusammensetzung – Basalt BM; TGL 23955/03.

1975b: Geologische Industrie – Gesteins-Standardproben – Chemische Zusammensetzung-Granite GM; TGL 23955/02

1975c: Geologische Industrie – Gesteins-Standardproben – Chemische Zusammensetzung-Tonschiefer TB; TGL 23955/04

Zentrales Geologisches Institut (cont.)

1975d: Geologische Industrie – Gesteins-Standardproben – Chemische Zusammensetzung-Schwarzschiefer TS; TGL 23955/06

1977a: Standardprobe Greisen GnA, Attestierte Gehalte der Komponenten; Stand 9/77.

1977b: Standardprobe Serpentinit SW, Attestierte Gehalte der Komponenten; Stand 9/77

APPENDIX

A stepwise procedure for the select laboratories method

PRINCIPLES

The "select laboratories method" is designed to approach the most probably correct value for the concentration of each constituent of proposed reference samples, where available results are dispersed over a broader range than would normally be expected from the imprecision of analytical methods. The method assumes that the work of some contributing laboratories is less subject to systematic error than is that of others.

Full application of the method is used only for constituents for which ten or more results have been reported. Where fewer than ten results are available, relatively uncertain estimates may be based on the median, as outlined below.

GENERAL STEPS

1. For each constituent of each sample, convert the reported values to the dry basis, using H_2O^- values (if any) reported at the same time. Where H_2O^- values are not available, assume all values to be already on the dry basis.
2. Arrange the results in descending order of magnitude, each identified with its contributing laboratory, for each constituent of each sample. (Where several results are reported from the same laboratory by different methods, by different analysts or at different times, such results must be considered as separate results.)

TREATMENT FOR FEWER THAN 10 RESULTS

3. If only one or two results are available, no usable value can be suggested.

*4. If three or four results are available, all in reasonable accord and determined by at least three mutually independent methods, report the median (M) as usable value, with a question mark to indicate uncertainty.

5. If five to nine results are available, regardless of disparities or methods used, report M, with a question mark, as usable value.

TREATMENT FOR 10 OR MORE RESULTS – LABORATORY RATING

6. Compute and record median (M), mean ($\bar{x}$) and standard deviation (s) for each constituent of each sample.
7. Score one point "poor" for each laboratory for each of its results (x) where $x < (\bar{x} - s)$ or $x > (\bar{x} + s)$.
8. For "x" values $(\bar{x} - s) < x < (\bar{x} + s)$, compute and record mean ($\bar{x}_1$) and standard deviation (s_1).
9. Score one point "fair" for each laboratory for each of its results (x) where $(\bar{x} - s) < x < (\bar{x}_1 - s_1)$ or $(\bar{x}_1 + s_1) < x < (\bar{x} + s)$.
10. Score one point "good" for each laboratory for each of its results (x) where $(\bar{x}_1 - s_1) < x < (\bar{x}_1 + s_1)$.
11. Using all the points scored for each laboratory for all constituents of all samples in the group, calculate the rating, R:

$$R = \frac{N_G - N_P}{N_G + N_F + N_P} \times 100,$$

where N_G = total number of good results,
N_F = total number of fair results, and
N_P = the total number of poor results.

12. Prepare a table, listing the laboratories in descending order of rating, showing the information in the example in Table 119. Note that the column headed N_T represents the totals of numbers of results reported by the individual laboratories; that headed Σ represents the cumulative totals of N_T.

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*(The asterisk at this step and at others indicates operations not amenable to automated computation.)

SELECT VALUES AND USABLE VALUES

13. As shown in Table 119, draw a broken line under the first laboratory whose Σ exceeds one-third of the Σ for the lowest laboratory. Draw a similar line over the first laboratory whose Σ exceeds one-half of the Σ for the lowest laboratory.

14. Consider all laboratories listed above the upper one of the two broken lines as "select".

15. Return to the tabulations of individual results in step 2, ignoring constituents for which fewer than 10 results are listed.

16. For each constituent of each sample, identify the results reported by the select laboratories (i.e. the "select values").

17. If the number of select values exceeds one half of the total number of results reported for a particular constituent, delete the value(s) reported by the select laboratory with the lowest rating, repeating the operation if necessary until the number of select values no longer exceeds one half of all values reported. (In cases where a particular laboratory has reported a large number of independent results, it may not be possible to meet this requirement.)

18. If the number of select values for a particular constituent is less than five, include the value(s) reported by the first laboratory below the upper broken line. If necessary, continue to add lower laboratories until at least five select values are found, but do not go below the lower broken line.

19. If only one or two select values are available after the preceding step, the median (M) of all original results for the constituent in that sample is taken as usable value, reported with a question mark.

20. Where three or four select values are available, record their median as usable value, with a question mark.

21. Where five or more select values are available, first check for the presence of outliers. An outlier is here defined as follows:

    In a set of values $x_1, x_2, x_3 \ldots. x_{(n-1)}, x_n$,

    x_1 is considered an outlier if $| x_1 - x_2 | \geq | x_2 - x_n |$;

    x_n is considered an outlier if $| x_n - (x_{(n-1)}) | \geq | x_{(n-1)} - x_1 |$.

    Reject any such outliers.

22. If step 21 reduces the number of select values (n_s) to four, proceed by step 18.

23. Calculate the median (M_s) and mean ($\bar{x}_s$) of the select values in each case.

24. Tabulate the values for M_s and $\bar{x}_s$ for all constituents of each sample, arranging the table as in Tables 9-30, 32-44, and 45-50 of this paper.

*25. With the tables of M_s and $\bar{x}_s$ side by side, choose one or the other of the two measures for each constituent, in order to bring the total closer to 100 per cent and to reduce the differences between Fe_2O_3TR and Fe_2O_3TC to a minimum. Subjective judgement is necessary because the two criteria for choice may be mutually contradictory. With ultrabasic rocks, for example, the apparent total is normally noticeably higher than 100 per cent, possibly because several elements included in the total as oxides may be present as free metals. When in doubt, favour M_s over $\bar{x}_s$.

26. Finally, tabulate all usable values in the form used in step 24.

Table 119. An example of rating listings

Lab No.	N_G	N_F	N_P	N_T	Σ	R	
9	9	0	0	9	9	100.0	
41	4	0	0	4	13	100.0	
30	1	0	0	1	14	100.0	
32	1	0	0	1	15	100.0	
43	24	8	1	33	48	69.7	
45	52	17	3	72	120	68.1	
36	4	2	0	6	126	66.7	
22	29	10	2	41	167	65.9	
47	98	22	12	132	299	65.2	
3	8	2	1	11	310	63.6	
34	9	1	2	12	322	58.3	
13	68	18	16	102	424	51.0	
5	28	16	4	48	472	50.0	
15	8	8	0	16	488	50.0	
27	51	17	13	81	569	46.9	
46	6	5	1	12	581	41.7	
35	156	59	47	262	843	41.6	
10	25	8	8	41	884	41.5	
21	43	23	12	78	962	39.7	(962 > (2693/3))
23	5	1	2	8	970	37.5	
2	199	92	68	359	1329	36.5	
16	21	15	6	42	1371	35.7	(1371 > (2693/2))
17	67	38	22	127	1498	35.4	
117	38	25	13	76	1574	32.9	
4	22	10	9	41	1615	31.7	
1	14	3	7	24	1639	29.2	
28	46	27	24	97	1736	22.7	
40	5	1	3	9	1745	22.2	
42	2	2	1	5	1750	20.0	
12	74	53	42	169	1919	18.9	
135	98	50	59	207	2126	18.8	
24	8	4	5	17	2143	17.6	
14	9	3	6	18	2161	16.7	
38	67	44	49	160	2321	11.2	
26	13	14	9	36	2357	11.1	
19	5	1	4	10	2367	10.0	
8	25	10	21	56	2423	7.1	
39	0	1	0	1	2424	0.0	
25	21	28	41	90	2514	-22.2	
102	38	34	107	179	2693	-38.5	

Table 120. XIGMR (China) Ultrabasic Rocks

pct (dry basis)	DZΣ-1	DZΣ-2
SiO_2	34.34	37.75
TiO_2	0.008	0.004
Al_2O_3	0.67	0.21
Fe_2O_3	4.21?	4.85?
FeO	2.42?	1.97?
MnO	0.068	0.097
MgO	41.03	38.34
CaO	0.10	1.80
Na_2O	0.008	0.028
K_2O	0.01	0.009
H_2O^+	14.17	12.69
CO_2	0.58	1.66
P_2O_5	0.004	0.003
S	0.051	0.008
Others	2.48	0.76
Sum	100.15	100.18
O/S, Cl	0.15	0.01
Sum (corr.)	100.00	100.17
Fe_2O_3T	6.90	7.04

	DZΣ-1		DZΣ-2	
	ppm	pct oxide	ppm	pct oxide
Cl	5700	0.57*	220	0.022*
Co (CoO)	94	0.012	100	0.013
Cr (Cr_2O_3)	10700	1.57	2900	0.42
Ir	0.003		0.003	
Ni (NiO)	2500	0.32	2400	0.30
Os	0.006		0.006	
Pd	0.005		0.002	
Pt	0.004		0.006	
Rh	0.0006		0.0012	
Ru	0.010		0.009	
V (V_2O_5)	39	0.007	17	0.003

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* Per cent element, not oxide